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**POSTULATES FOR ASSERTION, CONJUNCTION,  
NEGATION, AND EQUALITY**

**BY EDWARD V HUNTINGTON**



# POSTULATES FOR ASSERTION, CONJUNCTION, NEGATION, AND EQUALITY<sup>1</sup>

BY EDWARD V. HUNTINGTON

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## INTRODUCTION

The purpose of this paper is to present an "abstract deductive theory" so constructed that one of its "concrete interpretations" shall be a generalized form of the calculus of propositions in ordinary logic.

In the last analysis, every "abstract deductive theory" is a sequence of statements written down in a book by some human agent—each such statement being expressed in terms of some predetermined "base" or list of primitive symbols, and the steps by which later statements are derived from earlier ones being authorized by some pre-assigned list of "postulates".

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<sup>1</sup> Presented to the American Mathematical Society and the Association for Symbolic Logic at a joint session held in Cambridge, Massachusetts, September 1, 1936. An outline of part of this paper was printed (under the title Mathematical postulates for the logical operations of assertion, conjunction, negation, and equality) in the Proceedings of the National Academy of Sciences, vol. 22, pp. 291–296, May, 1936. (On p. 295, the theorem there numbered 51 should read,  $a^* \dashv Z^* = Z^*$ .)

The present theory may be regarded as a clarification and extension of C. I. Lewis's theory of "strict implication" (Lewis and Langford, Symbolic Logic, 1932). Professor Lewis has authorized and requested me to say that he accepts this presentation as a correct account of the formal properties of his system.

The use of the "subclass  $T$ " (corresponding roughly to the Frege assertion sign) was first suggested by the present writer in 1933 (Transactions Amer. Math. Soc., vol. 35, p. 291, 1933; see also Bull. Amer. Math. Soc., vol. 40, p. 127, 1934, and Fundamenta Mathematicae, vol. 25, pp. 147–156, 1935).

As to the equality sign, postulates for the symbol  $=$  regarded as a dyadic relation were given in my paper on "Effective equality and effective implication in formal logic," (Proc. Nat. Acad. Sci., vol. 21, pp. 266–271, 1935). In the present paper, the postulates for equality are given in terms of a new primitive symbol  $\equiv$  (read "quad"), which is a binary operator. The relation  $a = b$  is defined as meaning  $a \equiv b$  in  $T$ , so that the properties of the dyadic relation  $a = b$  are thrown back upon the postulated properties of the binary operator  $\equiv$  and the subclass  $T$ . The relation  $a = b$  thus becomes interpretable in the general sense of "interchangeability" (for any specified purpose) and not merely in the restricted sense of "mutual implication." Further, the

The "base" of the abstract deductive theory here considered is  $(K, T, \times, ', \equiv)$ , where  $K$  is a class of elements  $a, b, c, \dots$ ,  $T$  is a subclass in  $K$ ;  $\times$  (read "times") and  $\equiv$  (read "quad") are binary operators in  $K$ ; and  $'$  (read "dash") is a unary operator in  $K$ . (For brevity,  $ab$  will be written for  $a \times b$ )

The "postulates" of the theory are listed as Postulates 1-17, below. It is understood that the letters  $a, b, c, \dots$  are variables, each of which may stand for any element of  $K$ , that is, in any postulate or theorem, a letter such as  $a$  may be "replaced throughout" by any expression which stands for an element of  $K$ . ("Principle of substitution")

The notation  $X \rightarrow Y$  (read " $X$  leads to  $Y$ ") means "If, in the orderly development of the theory, we find the statement  $X$  already circularity in the use of the sign " $=$ " in Lewis's definition 11.08 is avoided, and the principle of "replacement of equals by equals," which is postulated as a rule of procedure by Lewis and subsequent writers (including B A Bernstein, E J Nelson, and others) is here deduced as a theorem. The symbol " $= Df$ " is not required. The concept " $a \equiv b$  in  $T$ " is similar to, though not quite the same as, the logogram " $|a = b|$ " introduced by A A Bennett and C A Baylis in their paper on "A calculus for propositional concepts" (Mind, vol 44, pp 152-167, 1935).

The postulates for Boolean algebra are adapted from my "fourth set" of 1933 (Trans. Amer. Math. Soc., vol 35, pp 280-284, with corrections on p 557 and p 971, see also Mind, vol 42, pp 203-207, 1933)

As to the central theorems 44 and 74, Th. 44 was first proved from Lewis's postulates in 1934 (Bull. Amer. Math. Soc., vol 40, pp 729-735, 1934). The fact that 74 follows from this proof as a corollary was communicated to me by Professor Lewis in October, 1934, and a simple proof of this fact was later given to me by W T Parry [An independent proof of 74 from Lewis's postulates is given by Tang Tsao-Chen (Bull. Amer. Math. Soc., vol 42, pp 743-746, 1936)]. The proof of 74 from our present postulates is much simpler than the earlier proofs, and requires no reference to Lewis's postulates.

The relation here called "Boolean implication,"  $ab = a$ , is the same as the relation called "effective implication" in my paper of 1935.

As to the examples for consistency and independence, the earliest example of a Lewis system with eight elements is due to W T Parry (Mind, vol 43, pp 78-80, 1934). Most of the other examples (including one with sixteen elements, and two that prove the independence of Lewis's Postulate B8) are new.

The last section presents a new direct comparison between the systems of "strict implication" and "material implication."

For the convenience of readers who may not have ready access to the earlier literature, all the proofs are given in full, so that the paper is entirely self-contained.

established, then we are authorized to write down the statement  $Y'$ . Thus the arrow,  $\rightarrow$ , is merely an abbreviation of language, and not one of the primitive concepts of the system. Obviously,  $X \rightarrow X$ . Also, if  $X \rightarrow Y$  and  $Y \rightarrow Z$ , then  $X \rightarrow Z$ . To indicate that both  $X \rightarrow Y$  and  $Y \rightarrow X$ , we write  $X \rightleftharpoons Y$ . (It should be noted that the arrow,  $\rightarrow$ , is used only between statements, not between elements of  $K$ .) Further, the notation " $X \& Y$ " means simply " $X$  and  $Y$ ", and the notation " $\exists a ( \quad )$ " means "there exists at least one element  $a$  such that ( )".

The theorems of the system are divided into two groups—those that are deducible from Postulates 1–14, and those that require for their proof one or more of the Postulates 15–17. Again, theorems (or postulates) which contain the arrow,  $\rightarrow$ , may be called "rules of procedure," as distinguished from "formal laws." (Since at least one rule of procedure is indispensable in any abstract deductive system, it appears to be largely a matter of taste how many such rules are admitted, either among the postulates or among the theorems.)

The "consistency" of the postulates is established by exhibiting finite examples of systems  $(K, T, \times, ', \equiv)$  which satisfy all the postulates. The (serial) "independence" of the postulates is established in a similar way, by exhibiting finite examples of systems  $(K, T, \times, ', \equiv)$  which satisfy some but not all of the postulates.

The "concrete interpretation" which is of chief interest is the system  $(K, T, \times, ', \equiv)$  exhibited in the example described as a generalized "calculus of propositions." But the question whether this (non-finite) example really does possess all the properties demanded by the postulates is a question of fact requiring a critical examination of the actual usages of language, and logicians may not all agree as to the linguistic facts. It is a virtue of the abstract formulation of the theory that it makes these debatable linguistic questions precise and definite, even though it does not pretend to answer them completely.

## §1 THE POSTULATES

*Base.  $(K, T, \times, ', \equiv)$  Language " $\rightarrow$ ", " $\&$ ", " $\exists$ "*

POSTULATE 1.  $a$  in  $K$  &  $b$  in  $K \rightarrow a \times b$  in  $K$  (Read  $a$  times  $b$ )

POSTULATE 2  $a$  in  $K \rightarrow a'$  in  $K$  (Read  $a$  dash)

POSTULATE 3  $a$  in  $K$  &  $b$  in  $K \rightarrow a \equiv b$  in  $K$  (Read  $a$  quad  $b$ )

POSTULATE 4 (a).  $a$  in  $T \rightarrow a$  in  $K$  ( $T$  a subclass in  $K$ )

(b)  $\exists a (a$  in  $T)$  ( $T$  non-empty)

(c)  $\exists a (a$  in  $K$  &  $a$  not in  $T)$  ( $T$  non-exhaustive)

These four postulates, 1-4, are "descriptive postulates," or "postulates of closure." They are all independent of each other. [But after any one of Postulates 11-14 is included, Postulate 4b may be replaced by the weaker form. ]  $a$  ( $a$  in  $K$ ), and Postulate 4c may be omitted altogether without seriously affecting the theory, as explained under Theorem 54c] The following postulates are understood to be required only in cases in which Postulates 1-4 are valid (As usual,  $ab$  is written for  $a \times b$ )

**POSTULATE 5**  $a$  in  $T$  &  $b$  in  $T \rightarrow ab$  in  $T$  (Rule of adjunction.)

**POSTULATE 6**  $ab$  in  $T \rightarrow a$  in  $T$  (Rule of reduction)

**DEFINITION A.**  $a = b \Leftrightarrow a \equiv b$  in  $T$  (Read  $a$  equal to  $b$ )

It should be noted that the symbol " $=$ " introduced by Definition A is part of the abstract system and has here no properties except such as are deducible from the postulates governing the symbols  $\equiv$  and  $T$ . The notation " $a = b$ " is merely a convenient abbreviation for the statement " $a \equiv b$  in  $T$ "

**POSTULATE 7**  $a$  in  $T$  &  $a = b \rightarrow b$  in  $T$  (Rule of equality for  $T$ )

**POSTULATE 8**  $a = b \rightarrow ac = bc$  (Rule of equality for  $\times$ )

**POSTULATE 9**  $a = b \rightarrow a' = b'$  (Rule of equality for  $'$ )

**POSTULATE 10**  $a = b \rightarrow (a \equiv c) = (b \equiv c)$  (Rule of equality for  $\equiv$ )

These ten postulates are "procedural postulates," since they involve the arrow,  $\rightarrow$  All the remaining postulates are "formal laws"<sup>2</sup>

**POSTULATE 11**  $(a \equiv b) = (b \equiv a)$  (Commutative law for  $\equiv$ )

**POSTULATE 12**  $ab = ba$  (Commutative law for  $\times$ )

**POSTULATE 13**  $(ab)c = a(bc)$  (Associative law for  $\times$ )

**POSTULATE 14**  $(a'b)'(a'b)' = a$  (Law of expansion.)

These postulates 5-14 are independent of each other, and of 1-4. The fourteen postulates 1-14 form the basis of Part I of our theory. In view of Theorem 33  $aa' = bb'$ , we are justified in introducing the following definition

**DEFINITION B**  $Z = aa'$  (Read the "zero element" of the system.)

---

\* It should be noted, however, that each of these formal laws is supposed to be preceded by the hypothesis that the letters involved are elements of  $K$ . For example, Postulate 12, when written out fully, should read:

$$a \text{ in } K \& b \text{ in } K \rightarrow ab \equiv ba \text{ in } T$$

In a sense, therefore, all the postulates, including the "formal laws," may be regarded as "rules of procedure," since they all involve the arrow

The remaining postulates (Part II) are understood to be required only in cases in which Postulates 1-14 are valid.

**DEFINITION C**  $a^* = (a \equiv Z)$

(Read "a star" Lewis's curl-diamond  $a$ )

**DEFINITION D**  $(a \dashv b) = (ab')^*$ .

(Read "a hook  $b$ " Lewis's "strict implication")

**POSTULATE 15**  $(a \dashv b)(b \dashv a) = (a \equiv b)$

(Law of equivalence "Mutual hook.")

**POSTULATE 16**  $[(a \dashv b)(b \dashv c) \dashv (a \dashv c)]$  in  $T$

(Law of the syllogism)

**POSTULATE 17**  $[a(a \dashv b) \dashv b]$  in  $T$

(Law of inference.)

These postulates 15-17 are independent of each other and of 1-14.

### §1a A POSSIBLE INTERPRETATION A GENERALIZED "CALCULUS OF PROPOSITIONS"

Before proceeding with the deduction of theorems, we mention at once the "concrete interpretation" which we have chiefly in mind. In this concrete system, the abstract symbols ( $K$ ,  $T$ ,  $\times$ ,  $', \equiv$ ) are interpreted as follows:

$K$  is the class of "propositions" (better described as "sentences").

$T$  is the subclass of propositions which are "asserted," so that the statement " $a$  is in  $T$ " means " $a$  is asserted."

$ab$  is the proposition known as the "logical product" (or "conjunction") of  $a$  and  $b$ , so that the statement " $ab$  is in  $T$ " means "the joint proposition,  $a$  and  $b$ , is asserted."

$a'$  is the proposition known as the "contradictory" of  $a$ , so that the statement " $a'$  is in  $T$ " means "the contradictory of  $a$  is asserted."

$a \equiv b$  is the proposition known as the "interchangeability" of  $a$  and  $b$  for some specified purpose, so that the statement " $a \equiv b$  is in  $T$ " means " $a$  is interchangeable with  $b$  for the purpose in hand."

Under this interpretation of the basic symbols ( $K$ ,  $T$ ,  $\times$ ,  $', \equiv$ ), the derived symbols introduced by Definitions B, C, D may be interpreted as follows:

$Z$  is "absurdity," that is,  $Z$  is the conjunction of any proposition with its contradictory. If  $Z$  were asserted, then every proposition would be asserted, which would be absurd.

$a^*$  is the proposition known as the "absurdity of  $a$ ," so that the statement " $a^*$  is in  $T$ ," or " $a \equiv Z$  is in  $T$ ," means "the absurdity of  $a$  is asserted," or " $a$  is absurd."

$a \rightarrow b$  is the proposition known as the "implication of  $a$  to  $b$ " so that the statement " $a \rightarrow b$  is in  $T$ " means " $a$  does imply  $b$ ."

As already intimated, the question whether this concrete system ( $K$ ,  $T$ ,  $\times$ , ',  $\equiv$ ) really does satisfy all the postulates is a question which belongs in the field of linguistics rather than in the field of mathematics, and will not be discussed in the present paper.

*An alternative example is obtained by replacing the word "asserted" by the word "demonstrable"*

Much simpler examples, containing only a finite number of elements, are given below (in order to establish the consistency and independence of the postulates). The reader may find it convenient to refer to Examples 01 and 06 at this point.

## §2 THEOREMS ON THE EQUALITY SIGN

Part I, depending only on Postulates 1-14, comprises Theorems 21-69. The theorems 21-29 develop the properties of the equality sign,  $=$ . In the proofs, the obvious properties of the arrow notation, and the use of Definition A, will be understood without special mention. (All the proofs are so arranged that the word "hence" refers to statements not more than two lines back.)

$$21 \quad ab \text{ in } T \rightarrow ba \text{ in } T$$

*Proof* By 7,  $ab$  in  $T \& ab \equiv ba$  in  $T \rightarrow ba$  in  $T$ . But by 12,  $ab \equiv ba$  in  $T$ . Hence  $ab$  in  $T \rightarrow ba$  in  $T$ .

$$22 \quad a \equiv b \text{ in } T \rightarrow b \equiv a \text{ in } T$$

*Proof* similar, 7, 11 being used in place of 7, 12.

$$23 \quad ab \text{ in } T \rightarrow b \text{ in } T$$

*Proof* By 21,  $ab$  in  $T \rightarrow ba$  in  $T$ . By 6,  $ba$  in  $T \rightarrow b$  in  $T$ . Hence,  $ab$  in  $T \rightarrow b$  in  $T$ .

$$24. \quad a = b \rightarrow ca = cb$$

*Proof* By 12 (and A),  $ac \equiv ca$  is in  $T$ .

By 10,  $ac \equiv ca$  in  $T \rightarrow (ac \equiv d) \equiv (ca \equiv d)$  in  $T$ .

Hence,  $(ac \equiv d) \equiv (ca \equiv d)$  is in  $T$ .

By 7,  $ac \equiv d$  in  $T \& (ac \equiv d) \equiv (ca \equiv d)$  in  $T \rightarrow ca \equiv d$  in  $T$ .

Hence,  $ac \equiv d$  in  $T \rightarrow ca \equiv d$  in  $T$ .

By 22,  $ca \equiv d$  in  $T \rightarrow d \equiv ca$  in  $T$ .

Hence,  $ac \equiv d$  in  $T \rightarrow d \equiv ca$  in  $T$

By 8,  $a \equiv b$  in  $T \rightarrow ac \equiv bc$  in  $T$

By (a),  $ac \equiv bc$  in  $T \rightarrow bc \equiv ca$  in  $T$

(a)

Hence,  $a \equiv b$  in  $T \rightarrow bc \equiv ca$  in  $T$

By (a),  $bc \equiv ca$  in  $T \rightarrow ca \equiv cb$  in  $T$

Hence,  $a \equiv b$  in  $T \rightarrow ca \equiv cb$  in  $T$  That is,  $a = b \rightarrow ca = cb$

$$25 \quad a = b \rightarrow (c \equiv a) = (c \equiv b)$$

Proof As in the proof of 24, using 11 in place of 12, we find  
 $(a \equiv c) \equiv d$  in  $T \rightarrow d \equiv (c \equiv a)$  in  $T$  (b)

Hence, using 10 and (b) in place of 8 and (a), we find  
 $a \equiv b$  in  $T \rightarrow (c \equiv a) \equiv (c \equiv b)$  in  $T$

$$26 \quad a = a \quad (\text{Law of identity})$$

Proof By 10,  $(a'b)'(a'b)' \equiv a$  in  $T \rightarrow [(a'b)'(a'b)' \equiv a] \equiv [a \equiv a]$  in  $T$   
 But by 14,  $(a'b)'(a'b)' \equiv a$  is in  $T$

Hence,  $[(a'b)'(a'b)' \equiv a] \equiv [a \equiv a]$  is in  $T$

Hence by 7,  $a \equiv a$  is in  $T$  That is,  $a = a$

$$27 \quad a = b \rightarrow b = a$$

Proof by 22 and A

$$28 \quad a = b \ \& \ b = c \rightarrow a = c$$

Proof By 10,  $a \equiv b$  in  $T \rightarrow (a \equiv c) \equiv (b \equiv c)$  in  $T$

By 22,  $(a \equiv c) \equiv (b \equiv c)$  in  $T \rightarrow (b \equiv c) \equiv (a \equiv c)$  in  $T$

Hence,  $a \equiv b$  in  $T \rightarrow (b \equiv c) \equiv (a \equiv c)$  in  $T$  (a)

From (a),  $a \equiv b$  in  $T \ \& \ b \equiv c$  in  $T \rightarrow b \equiv c$  in  $T \ \& \ (b \equiv c) \equiv (a \equiv c)$  in  $T$

By 7,  $b \equiv c$  in  $T \ \& \ (b \equiv c) \equiv (a \equiv c)$  in  $T \rightarrow a \equiv c$  in  $T$

Hence,  $a \equiv b$  in  $T \ \& \ b \equiv c$  in  $T \rightarrow a \equiv c$  in  $T$

That is, by A,  $a = b \ \& \ b = c \rightarrow a = c$

$$28a \quad a = b \ \& \ c = d \rightarrow ac = bd$$

Proof By 8, 24,  $a = b \ \& \ c = d \rightarrow ac = bc \ \& \ bc = bd$

By 28,  $ac = bc \ \& \ bc = bd \rightarrow ac = bd$

Hence,  $a = b \ \& \ c = d \rightarrow ac = bd$

$$28b \quad a = b \ \& \ c = d \rightarrow (a \equiv c) = (b \equiv d)$$

Proof by 10, 25, 28

In similar manner, every theorem authorizing the replacement of "equals by equals" which is required in this paper can be proved by direct deduction from the postulates. In order to avoid the labor of writing out the direct proof of each such theorem separately as needed, the following general theorem of replacement is here inserted. In establishing this general theorem, the indirect method of proof (reductio ad absurdum) is freely employed, but it should be clearly

noted that the indirect method of proof plays no essential part in the paper. The purpose of the general theorem is merely to convince the reader that each particular theorem can be proved directly if desired.

*29 Theorem of replacement* Let  $\xi$  be any expression which stands for an element of  $K$  (that is, any expression built up in accordance with Postulates 1, 2, 3, out of parentheses, the letters  $a, b, c, \dots$ , and the signs  $\times, ', \equiv$ ), and suppose that at some point in the expression  $\xi$  there occurs the letter  $a$ . Let  $\eta$  be another expression which differs from  $\xi$  only in having this particular  $a$  replaced by  $b$ . Then if we find  $a = b$  established, we are authorized to write down  $\xi = \eta$ . That is, when  $\xi$  and  $\eta$  have the meanings indicated, we have the theorem  $a = b \rightarrow \xi = \eta$ .

*Proof*<sup>4</sup> Let  $n$  be the number of marks (that is, parentheses, letters  $a, b, c, \dots$ , or signs  $\times, ', \equiv$ ) in the expression  $\xi$ . Then there are five possible cases to consider.

Case 1  $\xi$  may have the form of a product,  $\xi_1 m$ , where  $\xi_1$  is an expression involving the  $a$  in question and containing fewer than  $n$  marks, while  $m$  is an expression not involving the  $a$ . In this case  $\eta$  will have the form  $\eta_1 m$ , where  $\eta_1$  is the same as  $\xi_1$  with the  $a$  replaced by  $b$ , while  $m$  is unchanged. In this case we can prove that if the statement  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$  were false, then the statement  $a \equiv b$  in  $T \rightarrow \xi_1 \equiv \eta_1$  in  $T$  would also be false.

For, if this latter statement were true, then by 8 we would have  $a \equiv b$  in  $T \rightarrow \xi_1 \equiv \eta_1$  in  $T$ , that is,  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$ , contrary to the supposition.

Case 2  $\xi$  may have the form  $m\xi_1$ . In this case we can prove the same result, by using 24 instead of 8.

Case 3  $\xi$  may have the form  $\xi_2 \equiv m$ , where  $\xi_2$  involves the  $a$  in question and contains fewer than  $n$  marks, while  $m$  does not involve the  $a$ . In this case  $\eta$  will have the form  $\eta_2 \equiv m$ . In this case we can prove that if the statement  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$  were false, then the statement  $a \equiv b$  in  $T \rightarrow \xi_2 \equiv \eta_2$  in  $T$  would also be false.

For, if this latter statement were true, then by 10 we would have  $a \equiv b$  in  $T \rightarrow (\xi_2 \equiv m) \equiv (\eta_2 \equiv m)$  in  $T$ , that is,  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$ ; contrary to the supposition.

Case 4  $\xi$  may have the form  $m \equiv \xi_2$ . In this case we can prove the same result, by using 25 instead of 10.

---

<sup>4</sup> For a valuable suggestion in regard to this proof, I am indebted to Dr J. B. Rosser.

**Case 5**  $\xi$  may have the form  $(\xi_s)'$ , where  $\xi_s$  involves the  $a$  in question and contains fewer than  $n$  marks. In this case  $\eta$  will have the form  $(\eta_s)'$ , where  $\eta_s$  differs from  $\xi_s$  only in having the  $a$  replaced by  $b$ . In this case we can prove that if the statement  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$  were false, then the statement  $a \equiv b$  in  $T \rightarrow \xi_s \equiv \eta_s$  in  $T$  would also be false.

For, if this latter statement were true, then by 9 we would have  $a \equiv b$  in  $T \rightarrow (\xi_s)' \equiv (\eta_s)'$  in  $T$ , that is,  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$ , contrary to the supposition.

By successive applications of these five results, we can prove that if the statement  $a \equiv b$  in  $T \rightarrow \xi \equiv \eta$  in  $T$  were false, then the statement  $a \equiv b$  in  $T \rightarrow \xi_s \equiv \eta_s$  in  $T$  (where  $\xi_s$  has been reduced to the single element  $a$ , and  $\eta_s$  to the single element  $b$ ) would also be false. But this final statement,  $a \equiv b$  in  $T \rightarrow a \equiv b$  in  $T$ , is obviously true. Hence the supposition must have been false, and thus the theorem 29 is established.

*Note* These theorems 26, 27, 28, 29 show that within any system  $(K, T, \times, ', \equiv)$  which obeys Postulates 1-14, the sign " $=$ " introduced by Definition A may be handled exactly like the ordinary equality sign in mathematics. In what follows, free use will be made of this fact, without special mention on each occasion.

### §3 BOOLEAN ALGEBRA PROPERTIES

The five postulates 1, 2, 12, 13, 14, together with theorems 26-29, make the system a Boolean algebra with respect to  $(K, \times, ', \equiv)$ . Hence the following theorems, 31-39, may be classified as among the "Boolean algebra properties" of the system.

$$31 \quad a'' = a \quad (\text{Law of double negation})$$

*Proof.* By 14, 28a,  $aa' = [(a'a')'(a'a'')]' [(a''a'')'(a''a'')]'$

By 14, 28a,  $a'a'' = [(a''a')'(a''a'')]' [(a''a')'(a''a'')]'$

Hence by 12, 13,  $aa' = a'a''$ . Hence,  $a'a'' = a''a''$ .

By 14,  $a = (a'a')'(a'a'')$ . Hence,  $a = (a''a'')'(a''a'')$ .

By 14,  $a'' = (a''a')'(a''a'')$ . Hence by 12,  $a = a''$ .

$$32 \quad (ab)'(ab)' = a' \quad (\text{By 14, 31})$$

$$33 \quad aa' = bb'$$

*Proof* By 14, 32,  $aa' = [(a'b')'(a'b'')]' [(ab')'(ab'')]'$

By 14,  $bb' = [(b'a')'(b'a'')]' [(b''a')'(b''a'')]'$

Hence by 12, 13,  $aa' = bb'$

$$34. \quad \text{DEFINITION} \quad Z = aa'. \quad (\text{The "zero element" of the system.})$$

This definition is justified by theorem 33, which shows that  $aa'$  is a unique element in the system

$$35 \quad aZ' = a \quad (Z' \text{ is called the "universe element" of the system})$$

Proof By 32, 34,  $Z' = (ZZ)'(ZZ)' = (ZZ)'(Z)' \quad (\text{a})$

By 34, (a), 13, 12, 34,  $Z = ZZ' = Z(ZZ)'Z' = (ZZ)(ZZ)' = (Z)(ZZ)',$  whence by 13, 34,  $ZZ = Z[Z(ZZ)'] = (ZZ)(ZZ)' = Z \quad (\text{b})$

By (a), (b),  $Z' = Z'Z'. \quad (\text{c})$

By 14, 34, 12, 13, (c), 34, 14,

$$\begin{aligned} aZ' &= [(a'a')(a'a')']Z' = Z'(a'a')'Z' \\ &= (Z'Z')(a'a')' = Z'(a'a')' = (a'a')(a'a')' = a \end{aligned}$$

$$36 \quad aa = a \quad (\text{Idempotent law for } \times)$$

Proof By 35, 34, 32,  $(aa)' = (aa)'Z' = (aa)'(aa)' = a'$

Hence by 31,  $aa = a$

$$37 \quad aZ = Z$$

By 34, 13, 36, 34,  $aZ = a(aa') = (aa)a' = aa' = Z$

$$38 \quad a(a'b')' = a$$

Proof By 14, 13, 36, 14,

$$a(a'b')' = (a'b')(a'b')'(a'b')' = (a'b')(a'b')' = a$$

$$39 \quad a(b'c')' = [(ab)'(ac)']' \quad (\text{Distributive law for } \times)$$

Proof<sup>4</sup> By 32, 13,  $[a(b'c')']' = [a(b'c')'b]' [a(b'c')'b']' \quad (\text{a})$

By 12, 13, 38,  $a(b'c')'b = a[b(b'c')'] = ab \quad (\text{b})$

By 32, 12, 13, 14,

<sup>4</sup> If we introduce the following familiar definition

DEFINITION E  $a \vee b = (a'b')' \text{ (read } a \text{ wedge } b\text{), then we have at once the following five theorems, which make the system a Boolean algebra with respect to } (K, \vee, ') \text{.}$

$$(1) a \text{ in } K \& b \text{ in } K \rightarrow a \vee b \text{ in } K$$

$$(2) a \text{ in } K \rightarrow a' \text{ in } K$$

$$(3) (a \vee b) = (b \vee a) \quad (\text{Commutative law for } \vee)$$

$$(4) (a \vee b) \vee c = a \vee (b \vee c) \quad (\text{Associative law for } \vee)$$

$$(5) (a' \vee b')' \vee (a' \vee b)' = a \quad (\text{Law of expansion for } \vee)$$

From 38 and 39 we then have

$$a(a \vee b) = a$$

$$a(b \vee c) = ab \vee ac \quad (\text{Distributive law for } \times)$$

$$a \vee bc = (a \vee b)(a \vee c) \quad (\text{Distributive law for } \vee)$$

<sup>4</sup> For a marked simplification of my 1938 proof of this theorem 39, I am indebted to Professor A. A. Bennett

$$a(b'c')'b' = a(b'c')'[(bc)'(bc')'] = a[(c'b)'(c'b')'](bc)' = ac(bc)' \quad (\text{c})$$

$$\text{By (b), (c) in (a), } [a(b'c')]' = (ab)'[ac(bc)']' \quad (\text{d})$$

$$\text{From (d), } [a(c'b')]' = (ac)'[ab(cb)']', \quad (\text{e})$$

$$\text{whence by 12, } [a(b'c')]' = (ac)'[ab(bc)']'$$

By 36, (d), (e), 12, 13, 31, 38, 38,

$$\begin{aligned} [a(b'c')]' &= [a(b'c')'][a(b'c')]' = \\ &= (ab)'[ac(bc)']'(ac)'[ab(bc)']' = \\ &= (ab)'[(ab)''(bc)']'(ac)'[(ac)''(bc)']' = \\ &= (ab)'(ac)' \end{aligned}$$

Hence by 31,  $a(b'c')' = [(ab)'(ac)']'$

#### §4 "BOOLEAN" IMPLICATION

The following theorems, 41–49, are also "Boolean algebra properties" of the system

$$41 \quad ab' = Z \Leftrightarrow ab = a$$

**Proof** By 39, 34, 35,

$$b'(a''b')' = [(b'a')'(b'b)']' = [(b'a')'Z']' = [(b'a')']', \quad (\text{a})$$

$$\text{whence by 31, 12, } b'(ab')' = a'b' \quad (\text{b})$$

$$\text{By 31, 35, } ab = a[b']' = a[b'(Z)']' \quad (\text{c})$$

$$\text{By 38, (a), } a = a[a'b']' = a[b'(ab')']' \quad (\text{d})$$

From (b), (c),  $ab' = Z \rightarrow ab = a$ , which is the first part of the theorem

$$\text{By 38, 31, 12, 13, } ab' = a[b'(b'a')] = b'[a(ab)'] \quad (\text{e})$$

$$\text{By 37, } Z = b'Z = b'[a(a)'] \quad (\text{f})$$

From (d), (e),  $ab = a \rightarrow ab' = Z$ , which is the second part

$$42 \quad a'b' = b' \Leftrightarrow ab = a$$

**Proof** By 31,  $ab = a(b')'$  By 38,  $a = a(a'b')'$

Hence,  $a'b' = b' \rightarrow ab = a$ , which is the first part

$$\text{By 38, 31, 12, } b' = b'(b'a')' = b'(ab)' \quad \text{By 12, } a'b' = b'(a)'.$$

Hence,  $ab = a \rightarrow a'b' = b'$ , which is the second part

$$43 \quad \text{DEFINITION } a \leq b \Leftrightarrow ab' = Z \quad (\text{Read } a \text{ implies } b)$$

$$44. \quad a \leq b \Leftrightarrow ab = a \quad (\text{By 43, 41})$$

This relation,  $a \leq b$ , has the fundamental properties commonly associated with the word "implication," as follows

$$45 \quad a \leq a. \quad (\text{Self-implication})$$

**Proof** by 44, 36, 26

$$46. \quad a \leq b \Leftrightarrow b' \leq a' \quad (\text{Inverse implication})$$

Proof by 43, 31, 12

$$47 \quad a \leq b \ \& \ b \leq c \Rightarrow a = b \quad (\text{Mutual implication, or equivalence})$$

Proof by 44, 12

$$48 \quad a \leq b \ \& \ b \leq c \rightarrow a \leq c \quad (\text{Syllogism})$$

Proof. By 44, 43, 28a, 13, 36, 37, 44, 43,  
 $a \leq b \ \& \ b \leq c \rightarrow ab = a \ \& \ bc' = Z \rightarrow abc' = aZ \rightarrow (ab)c' = Z \rightarrow (a)c' = Z \rightarrow a \leq c$

$$49 \quad a \text{ in } T \ \& \ a \leq b \rightarrow b \text{ in } T \quad (\text{Inference})$$

Proof By 44, 27, 7, 23,

$$a \text{ in } T \ \& \ a \leq b \rightarrow a \text{ in } T \ \& \ a = ab \rightarrow ab \text{ in } T \rightarrow b \text{ in } T$$

The following theorem will be useful in the proof of 59.

$$49a \quad ab = Z \ \& \ a'b' = Z \rightarrow b = a'$$

Proof By 41, 31,  $ab = Z \rightarrow ab' = a$ ,

and by 41, 12,  $a'b' = Z \rightarrow ab' = b'$ . Hence the theorem.

### §5 ASSERTED AND REJECTED ELEMENTS. THE SUBCLASS $T'$

The theorems of this section (51–59), like all the preceding theorems, depend only on Postulates 1–14 (Note that 52c and 54c, together with Postulate 4c, may all be omitted, if preferred, in view of 55.)

51  $Z'$  is in  $T$

Proof By 7,  $a$  in  $T \ \& \ a = aZ'$  in  $T \rightarrow aZ'$  in  $T$

But by 35, 27,  $a = aZ'$  is in  $T$ . Hence  $a$  in  $T \rightarrow aZ'$  in  $T$ .

By 23,  $aZ'$  in  $T \rightarrow Z'$  in  $T$ . Hence,  $a$  in  $T \rightarrow Z'$  in  $T$

That is, if there is any element in  $T$ , then  $Z'$  is in  $T$ . But by 4b, there is at least one element  $a$  such that  $a$  is in  $T$ . Hence  $Z'$  is in  $T$ .

52  $Z$  in  $T \rightarrow b$  in  $T$ , whence

52c  $Z$  is not in  $T$

Proof. By 34,  $Z$  in  $T \rightarrow bb'$  in  $T$ . By 6,  $bb'$  in  $T \rightarrow b$  in  $T$ . Hence,  $Z$  in  $T \rightarrow b$  in  $T$

That is, if  $Z$  is in  $T$ , then every element of  $K$  is in  $T$ . But by 4c, there exists at least one element of  $K$  which is not in  $T$ . Hence,  $Z$  is not in  $T$ .

The significance of these two theorems will be made clearer if we introduce the following definition of a new subclass,  $T'$

53 DEFINITION  $a$  in  $T' \Leftrightarrow a'$  in  $T$  (Read.  $a$  in  $T$  dash)

The statement  $a$  in  $T'$  must not be confused with the statement  $a$  not in  $T$ .

If we think of  $T$  as the class of "asserted" elements, and of  $a'$  as the element "contradictory" to  $a$ , then we may conveniently speak of  $T'$  as the class of "rejected" elements, but if this terminology is used, it must be clearly understood that a "rejected" element means precisely what definition 53 says it means, namely "an element whose contradictory is asserted," and not merely "an element which itself is not asserted." But there may be many elements of  $K$  which are not in  $T$  and also not in  $T'$ —that is, many elements which are neither "asserted" nor "rejected."

In this connection, it should be especially noted that the concept of "class," as a "completed totality of elements" plays no part in the theory of the present paper. Concerning any given object, we are supposed to be able to tell whether or not it has the property described by the phrase "in  $K$ ", and concerning any element of  $K$  (that is, any object having the property "in  $K$ "), we are supposed to be able to tell whether or not it has the further property described by the phrase "in  $T$ ", but while it is convenient to speak of  $K$  and  $T$  as "classes," they may be more properly regarded as "predicates," since the technical "theory of classes" is not involved at any point.

The following theorem states merely that no element  $a$  can have both the properties  $T$  and  $T'$ .

54  $a$  in  $T$  &  $a$  in  $T' \rightarrow b$  in  $T$ , whence,

54c  $a$  in  $T \rightarrow a$  not in  $T'$ , and  $a$  in  $T' \rightarrow a$  not in  $T$

**Proof** By 53, 5, 52,

$a$  in  $T$  &  $a$  in  $T' \rightarrow a$  in  $T$  &  $a'$  in  $T \rightarrow aa'$  in  $T \rightarrow Z$  in  $T \rightarrow b$  in  $T$ . That is, if  $a$  and  $a'$  are both in  $T$ , then every element of  $K$  is in  $T$ . But by 4c, there exists at least one element of  $K$  which is not in  $T$ . Hence the supposition  $a$  in  $T$ , &  $a$  in  $T'$  cannot hold. Hence,  $a$  in  $T \rightarrow a$  not in  $T'$ , and  $a$  in  $T' \rightarrow a$  not in  $T$ .

55. Note. If one prefers to avoid the use of the word "not" in the formal theory, one may omit Postulate 4c and Theorem 52c and 54c, replacing them by the non-formal theorem  $Z$  in  $T \rightarrow T = K$ " (where the notation " $T = K$ " means that the classes  $T$  and  $K$  coincide), together with the convention that the case " $T = K$ ", while formally admissible, is to be regarded as practically trivial.

56  $Z$  is in  $T'$

**Proof** by 51, 53.

57.  $Z \leq a$

**Proof.** By 37, 44, 29,  $Z = Z$  in  $T \rightarrow Za = Z$  in  $T \rightarrow Za = Z \rightarrow Z \leq a$

But by 26,  $Z \equiv Z$  is in  $T$ . Hence  $Z \leq a$ . That is, the zero element "implies" every element.

Note This theorem 57 ( $b = Z \rightarrow b \leq a$ ) must not be confused with the paradoxical proposition 57a  $b$  in  $T' \rightarrow b \leq a$ . This latter proposition ("a rejected element implies every element") cannot be proved from our postulates.

$$58 \quad a \leq Z'$$

Proof By 35, 44, 29,  $a \equiv a$  in  $T \rightarrow aZ' \equiv a$  in  $T \rightarrow aZ' = a \rightarrow a \leq Z'$ . But by 26,  $a \equiv a$  is in  $T$ . Hence  $a \leq Z'$ . That is, the universe element is "implied by" every element.

Note This theorem 58 ( $b = Z' \rightarrow a \leq b$ ) must not be confused with the paradoxical proposition 58a  $b$  in  $T \rightarrow a \leq b$ . This latter proposition ("an asserted element is implied by every element") cannot be proved from our postulates.

The following theorem concerns the number of elements ( $2^n$ ) in a finite Boolean algebra.

59 (1) Any class  $K$  containing  $2^n$  elements ( $n = 1, 2, 3, \dots$ ) can be made into a Boolean algebra  $(K, \times, ')$  by suitably defining the binary operator "times" and the unary operator "dash", and (2) in any finite Boolean algebra  $(K, \times, ')$  the number of elements is some power of 2. (The degenerate case where  $K$  contains only a single element may be included under the name Boolean algebra if desired<sup>6</sup>.)

Proof of (1) Following a device due to H. M. Sheffer (1920), let  $K$  be represented as the class of all factors of a "Boolean integer,"  $B$ , where a Boolean integer means any integer which has no repeated factor (other than 1). For example, if  $B = 210$ , then  $K =$

$$1, 2, 3, 6, 5, 10, 15, 30, 7, 14, 21, 42, 35, 70, 105, 210$$

(Since the introduction of each new prime doubles the number of elements, any such class  $K$  will clearly contain  $2^n$  elements.) Now let  $ab =$  the least common multiple of  $a$  and  $b$ , and let  $a' =$  the quotient of  $B$  divided by  $a$ . Then it is readily seen that Postulates 1, 2, 12, 13, 14 are all satisfied. (Here  $Z = B$  itself, and  $a \leq b$  means "a contains  $b$  as a factor".)

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<sup>6</sup> H. M. Stone, Postulates for Boolean algebras and generalized Boolean algebras, Amer. Journal of Math., vol. 57, pp. 703-732, 1935, especially page 705.

**Proof of (2)**<sup>7</sup> In this proof we use the notation " $a \neq b$ " for " $a = b$  does not hold," and introduce the definition of a "prime" element as follows

**DEFINITION** A "prime" element  $p$  is any element which occurs not more than three times in the table for  $ab$ . That is, if  $p$  is prime, then  $pb = p \rightarrow (b = Z' \text{ or } b = p)$ , and if  $a$  is not prime, then  $\exists b (b \neq Z', b \neq a) ab = a$ . (Compare the table for  $ab$  in Example 0.6, below, where the prime elements, other than  $Z'$ , are 2, 3, 5, 9.)<sup>8</sup>

On the basis of this definition, we prove the following lemmas

**Lemma 1** If  $p, q$  are distinct primes, then  $p'q' = Z$

**Proof** Let  $c' = p'q'$ . Then by 38,  $pc = p(p'q')' = p$ , whence, by the definition of prime,  $c = Z'$  or  $c = p$ . Similarly,  $qc = q$ , whence  $c = Z'$  or  $c = q$ . But by hypothesis,  $p \neq q$ . Hence  $c = Z'$ , that is,  $p'q' = Z$ .

**Lemma 2** If  $u = pqr$  and  $v = st$ , then  $u'v' = Z$ . Here  $p, q, r$ , are distinct primes  $\neq Z'$ , and  $s, t$ , are a second set of distinct primes  $\neq Z'$ , entirely distinct from the first set,  $u$  = the product of one or more factors from the first set, and  $v$  = the product of one or more factors from the second set. (Similarly, we may let  $w$  = the product of one or more factors from a third set having nothing in common with either of the other two sets.)

**Proof** By successive applications of 39 we find

$$\begin{aligned} u'v' &= (pqr)'(st)' \\ &= [(p's)'(p't)']'(q'r)'(q't)'], \text{ whence} \\ \text{by Lemma 1, } u'v' &= [Z'Z' Z'Z']' = [Z']' = Z \end{aligned}$$

<sup>7</sup>This proof will be found easier to follow than the proof given in my paper of 1904 (Trans Amer Math Soc, vol 5, p 309). Another proof, more closely connected with the theory of "lattices" (Garrett Birkhoff, H M MacNeille, etc.), has been pointed out to me by Saunders MacLane as a corollary of his paper "On the representation of finite lattices," presented to the Amer Math Soc on March 30, 1934.

<sup>8</sup>If  $p$  is a prime element, then  $p'$  may be called a "basic" element. Thus, in Example 0.6, the basic elements, besides  $Z$ , are 15, 14, 12, 8. If  $K$  is represented as a finite class of regions in a square, with  $ab$  = the region common to the regions  $a$  and  $b$ , and  $a'$  = the region complementary to the region  $a$ , then the prime elements are the "large" regions (including the whole square,  $Z'$ ), while the basic elements are the "small" regions (including the null region,  $Z$ ), and  $a \leq b$  means " $a$  within  $b$ ". The basic elements bear the same relation to the operator  $\vee$ , that the prime elements bear to the operator  $\times$ . (The "principle of duality")

**Lemma 3** With the same notation as in Lemma 2 we have

$$uv \neq Z', \quad v \neq u, \quad uv \neq u, \quad \text{and} \quad uv \neq uw$$

**Proof** Suppose  $u = Z'$ , that is,  $pqr = Z'$ , then by 35, 37, 13,  $p' = p'Z' = p'(pqr) = Z(qr) = Z$ , whence  $p = Z'$ , contrary to hypothesis. Again, suppose  $v = u$ , then by 36 and Lemma 2,  $u' = u'v = Z$ , contrary to result just proved. Again, suppose  $uv = u$ , then by 42 and Lemma 2,  $v' = u'v' = Z$ , whence  $v = Z'$ , contrary to result just proved. Again, suppose  $uv = uw$ , then by 36, 39, and Lemma 2,  $(uv)' = (uw)'(uw)' = [(u'u')'(u'w')'(v'u')'(v'w')]' = u'$ , whence  $uv = u$ , contrary to result just proved.

**Lemma 4** If  $uv = Z$ , then  $v = u'$ . (Same notation as in Lemma 2)

**Proof** By Lemma 2,  $u'v' = Z$ , and by 49a,  $uv = Z \& u'v' = Z \rightarrow v = u'$ .

**Lemma 5** In a finite Boolean algebra, if  $a$  is not prime, then  $a \leq p$ , where  $p$  is a prime  $\neq Z'$

**Proof** By 44 and the definition of prime,  $\exists b(b \neq Z', b \neq a) \cdot a \leq b$ . If  $b$  is not prime,  $\exists c(c \neq Z', c \neq b) \cdot b \leq c$ , and by 48, 47,  $c \neq a$ . If  $c$  is not prime,  $\exists d(d \neq Z', d \neq c) \cdot c \leq d$ , and by 48, 47,  $d \neq b, d \neq a$ . This process leads to a chain of non-primes,  $a \leq b \leq c \leq d \leq \dots$ , each element of the chain being distinct from all its predecessors. Hence, since  $K$  is finite, we must finally reach an element  $p$  which is prime, whence by 47,  $a \leq p$ .

**Lemma 6** In a finite Boolean algebra, if  $a$  is not prime, then  $a = pb$ , where  $p$  is a prime  $\neq Z'$ , and  $b \neq a$ .

**Proof** By Lemma 5,  $\exists p(p \neq Z') \cdot a \leq p$ , whence by 44, 42,  $ap = a$  and  $a'p' = p'$ . Let  $b = (a'p)'$ . Then by 39,  $pb = p(a'p)' = [(pa)'(pp')]' = pa = a$ . Also,  $b \neq a$ . For if  $b = a$ , then  $a = (a'p)'$ , whence by 42,  $ap' = p'$ , whence  $p' = p'p' = (ap')(a'p') = aa'pp' = Z$ , contrary to the fact that  $p \neq Z'$ .

**Lemma 7** In a finite Boolean algebra, any element  $a$  can be expressed as the product of a finite number of distinct primes.  $a = Z'pqr \dots$

**Proof** If  $a$  is not prime, then by Lemma 6,  $a = pb$ , where  $b \neq a$ . If  $b$  is not prime, then by Lemma 6,  $b = qc$ , where  $c \neq b$ , so that  $a = pqc$ . Also,  $c \neq a$ . (For, if  $c = a$ , then  $b = qa$  while  $a = pb$ , whence by 44,  $b \leq a$  and  $a \leq b$ , whence by 48,  $a = b$ , contrary to fact.) If  $c$  is not prime, then by Lemma 6,  $c = rd$ , where  $d \neq c$ , so that  $a = pqrdrd$ . Also,  $d \neq b$  and  $d \neq a$ . (For, if  $d = b$ , then  $c = rb$  while  $b = qc$ , whence  $c \leq b$ ,

and  $b \leq c$ , whence  $b = c$ , contrary to fact, and if  $d = a$ , then  $c = ra$ , while  $a = pqc$ , whence  $c \leq a$  and  $a \leq c$ , whence  $a = c$ , contrary to fact.) This process leads to a sequence of distinct primes,  $a = pqr$ . which must terminate, since  $K$  is finite.

**Lemma 8** If a finite Boolean algebra  $(K, \times, ')$  has exactly  $n$  prime elements,  $p, q, r, \dots$ , then it will have exactly  $2^n$  elements in all, namely.

$$Z', p, q, pq, r, pr, qr, pqr, s, ps, qs, pqs, rs, prs, qrs, pqrss.$$

**Proof.** By Postulate 1 and Lemma 3, all these  $2^n$  elements exist and are distinct; and by Lemma 7, each element  $a$  will find its place somewhere in this list. In particular,  $Z =$  the product of all the  $n$  primes. (For, if  $Z = pq$ , say, with  $r$  omitted, then  $pqr = Zr = Z$ , and  $pqr$  would not be distinct from  $pq$ .) Hence, by Lemma 4, if  $a$  is the  $k$ th element from one end of the list, then  $a'$  will be the  $k$ th element from the other end of the list, so that no further elements are introduced by Postulate 2.

By this Lemma 8, Theorem 59 (2) is established

### §6 INTRODUCTORY PROPERTIES OF $a^*$ AND $a \dashv b$

The theorems of this section, 61–69, depend only on Postulates 1–14, their chief interest, however, is to serve as an introduction to the theorems of Part II.

**61 DEFINITION**  $a^* = a \equiv Z$  (Read a star)

In particular,  $Z^* = Z \equiv Z$ .

**62 DEFINITION**  $a \dashv b = (ab')^*$  (Read a hook  $b$ )

**62a.**  $a \dashv b = ab' \equiv Z$  (By 61, 62)

**62b.**  $a \dashv b$  in  $T \dashv a \leq b$  (By 43, 62a.)

**63 (1).**  $a \dashv a' = a^*$  (By 62, 36)

**(2)**  $a \dashv Z = a^*$ . (By 62, 35)

**64 (1).**  $Z^*$  is in  $T$  (By 61, A, 26)

**(2).**  $a^*$  in  $T \rightarrow a = Z$ . (By 61, A)

**(3).**  $a = b \rightarrow a^* = b^*$ . (By 61, 10)

**(4).**  $a^* = Z^* \rightarrow a = Z$  (By 64 (1), 64 (2))

**65 (1).**  $a \dashv a = Z^*$  (By 62, 34.)

**(2)**  $Z \dashv a = Z^*$  (By 62, 37)

**(3)**  $a \dashv Z' = Z^*$ . (By 62, 31, 37)

**66.**  $ab \dashv a = Z^*$ . (By 62, 13, 34, 37.)

$$67 \quad a \dashv ab = a \dashv b$$

**Proof.** By 62, 31, 39, 34, 35, 31, 62,  
 $a \dashv ab = [a(a''b'')]^* = [(aa')(ab')']^* = [(ab')']^* = (ab')^* = a \dashv b$ .

$$68 \quad a \dashv b = b' \dashv a'$$

**Proof.** By 62, 31, 12, 62,  $a \dashv b = (ab')^* = (b'a'')^* = b' \dashv a'$

$$69 \quad (a \dashv b) \text{ in } T \rightarrow (a \dashv b) = Z^*$$

**Proof** By 62a, 64 (3), 62,  
 $(a \dashv b) \text{ in } T \rightarrow ab' = Z \rightarrow (ab')^* = Z^* \rightarrow (a \dashv b) = Z^*$ .

This theorem 69, in view of 64 (1), shows that among all the elements of  $T$ , the only one which can appear in a table for  $a \dashv b$  is the element  $Z^*$  (Compare 71)

### §7. THEOREMS REQUIRING THE USE OF POSTULATE 15

The preceding theorems have all been proved on the basis of Part I, that is, Postulates 1-14. We now turn to the theorems of Part II, which require for their proof one or more of the Postulates 15-17, which are characteristic of Lewis's theory of strict implication.

Theorems 71-75 depend on 1-14 and 15. They cannot be proved from 1-17 if 15 is omitted (See Example 15.)

$$71 \quad (a \equiv b) \text{ in } T \rightarrow (a \equiv b) = Z^*$$

**Proof** By A, 8, 34, 64 (3), 62,

$$(a \equiv b) \text{ in } T \rightarrow a = b \rightarrow ab' = bb' \rightarrow (ab')^* = Z^* \rightarrow (a \dashv b) = Z^*$$

Hence by 11,  $(a \equiv b) \text{ in } T \rightarrow (b \dashv a) = Z^*$ . Hence by 28a, 15, 36,

$$(a \equiv b) \text{ in } T \rightarrow (a \dashv b)(b \dashv a) = Z^*Z^* \rightarrow (a \equiv b) = Z^*$$

This theorem 71, in view of 64 (1), shows that among all the elements of the subclass  $T$ , the only one which can appear in a table for  $a \equiv b$  is the element  $Z^*$  (Compare 69.)

$$72 \quad a \equiv a = Z^*$$

**Proof.** By 15, 65 (1), 36,  $a \equiv a = (a \dashv a)(a \dashv a) = Z^*Z^* = Z^*$

$$73 \quad a^*Z^* = a^*$$

**Proof** By 63 (2), 65 (2), 15, 61,  $a^*Z^* = (a \dashv Z)(Z \dashv a) = a \equiv Z = a^*$ .

$$74 \quad a \dashv b = ab \equiv a$$

**Proof** By 15, 66, 67, 62, 73, 62,

$$(ab \equiv a) = (a \dashv ab)(ab \dashv a) = (a \dashv b)Z^* = (ab')^*Z^* = (ab')^* = a \dashv b$$

This important theorem establishes the complete equivalence between Lewis's "strict" implication ( $ab' \equiv Z$ ) and our "Boolean" implication ( $ab \equiv a$ ). While Theorem 44 ( $a \leq b \Leftrightarrow ab = a$ ) is an immediate consequence of Theorem 74 ( $a \dashv b = ab \equiv a$ ), it should be noted that 74 cannot be deduced from 44 without the aid of 15.

$$75 \quad a^* \dashv Z^* = Z^*$$

**Proof** By 74, 73, 72,  $a^* \dashv Z^* = a^*Z^* \equiv a^* = a^* \equiv a^* = Z^*$

The following theorem 78 depends on 1-14 and 15 and 16. It cannot be proved from 1-17 without 15, and it cannot be proved from 1-17 without 16. (See Examples 15, 16.)

$$78 \quad a^* \dashv (ab)^* = Z^*$$

**Proof** By 65 (2),  $Z \dashv a = Z \dashv b'$ . Hence by 61, 15,  $a^* = a \equiv Z = (a \dashv Z)(Z \dashv a) = (a \dashv Z)(Z \dashv b')$ . By 62, 31,  $(ab)^* = (a \dashv b')$ . Hence,  $a^* \dashv (ab)^* = (a \dashv Z)(Z \dashv b') \dashv (a \dashv b')$ , which by 16 is in  $T$ . Hence,  $a^* \dashv (ab)^*$  is in  $T$ . Hence by 69,  $a^* \dashv (ab)^* = Z^*$ .

### §8 THEOREMS REQUIRING THE USE OF POSTULATE 17

The six following theorems, 81-86, depend on Postulates 1-14 and 17. They cannot be proved from 1-17 without the use of 17. (See Example 17.)

$$81 \quad a(a \dashv b) \dashv b = Z^* \quad (\text{By } 17, 69)$$

$$82 \quad a^*a = Z$$

**Proof** By 36, 12, 13, 31, 62, 63 (1), 81,  
 $(a^*a)^* = [a^*(aa)]^* = [(aa^*)a']^* = aa^* \dashv a' = a(a \dashv a') \dashv a' = Z^*$   
Hence by 64 (4),  $a^*a = Z$

$$83 \quad a^* \dashv a' = Z^* \quad (\text{By } 62, 31, 82)$$

$$84 \quad Z'^* = Z$$

**Proof** By 17,  $Z'(Z' \dashv Z) \dashv Z$  is in  $T$ . Hence by 35,  $(Z' \dashv Z) \dashv Z$  is in  $T$ . Hence by 63 (2),  $Z'^* \dashv Z$  is in  $T$ . Hence by 63 (2),  $Z'^{**}$  is in  $T$ . Hence by 64 (2),  $Z'^* = Z$

$$85 \quad Z' \dashv Z = Z \quad (\text{By } 62, 36, 84)$$

$$86 \quad a(a^{**}) = a$$

**Proof** By 43, 44,  $ab' = Z \rightarrow ab = a$ . Hence,  $a(a^{**})' = Z \rightarrow a(a^{**}) = a$ . But by 31, 82,  $a(a^{**})' = aa^* = Z$ . Hence,  $a(a^{**}) = a$ .

The following Theorem 87 depends on 1-14 and 15 and 17. It cannot be proved from 1-17 without 15; and it cannot be proved from 1-17 without 17. (See Examples 15, 17.)

$$87 \quad Z^{**} = Z.$$

Proof By 61, 15, 63 (2), 65 (2), 82,  
 $Z^{**} = Z^* \equiv Z = (Z^* \dashv Z)(Z \dashv Z^*) = Z^{**}Z^* = .Z$

### §9 LEWIS'S POSTULATES ON THE BASE ( $K, T, \times, ', ^*$ )

In Lewis's own presentation of his theory, the "undefined ideas" are, in our notation,  $K, T, \times, ', ^*$ . Here  $K$  is a class of elements  $a, b, c, \dots$ ,  $T$  is a subclass in  $K$ ,  $\times$  (read "times") is a binary operator,  $'$  (read "dash") is a unary operator, and  $*$  (read "star") is another unary operator [The binary operator which we have denoted by  $\equiv$  (read "quad") is introduced by definition, as is the binary operator  $\dashv$  (read "hook")]

The relation of interchangeability,  $a = b$ , is treated as part of ordinary language, like  $\rightarrow$ ,  $\&$ , and  $\exists$ . The properties of the equality sign " $=$ " which we have deduced in Theorems 26, 27, 28 are treated as part of the language, and our Theorem 29 (the "Theorem of Replacement") is postulated as a rule of procedure [Lewis and Langford, Symbolic Logic, page 125, (b)]. The Principle of Substitution for variables is of course assumed [page 125, (a)], as well as (tacitly) the usual postulates of closure [page 189, footnote].

Besides the principle of substitution, Lewis's list, in our notation, is as follows (on the base  $K, T, \times, ', ^*$ ).

POSTULATE 1.  $a$  in  $K \& b$  in  $K \rightarrow ab$  in  $K$  [By 1.]

POSTULATE 2.  $a$  in  $K \rightarrow a'$  in  $K$  [By 2.]

POSTULATE 3a.  $a$  in  $K \rightarrow a^*$  in  $K$ . [By 3, Def C]

POSTULATE 4 (a)  $a$  in  $T \rightarrow a$  in  $K$  [By 4.]

(b)  $\exists a$  ( $a$  in  $T$ )

(c)  $\exists a$ . ( $a$  in  $K$ . &  $a$  not in  $T$ )

DEFINITION Df2.  $a \dashv b = .(ab)^*$  [By Def D]

DEFINITION Df3.  $a \equiv b = (a \dashv b)(b \dashv a)$  [By 15.]

RULE OF REPLACEMENT.  $(a \dashv b)(b \dashv a)$  in  $T \dashv a = b$

That is, if  $(a \dashv b)(b \dashv a)$ , or  $a \equiv b$ , is in  $T$ , then either of the two elements  $a$  and  $b$  may be replaced by the other at any point of any formula of the system [By Def A and Th 29]

RULE OF ADJUNCTION.  $a$  in  $T \& b$  in  $T \rightarrow ab$  in  $T$  [By 5.]

RULE OF INFERENCE  $a$  in  $T$ . &  $a \dashv b$  in  $T \rightarrow b$  in  $T$  [By 62(b), 49]

POSTULATE B1.  $ab \dashv ba$  in  $T$ . [By 12, 65 (1), 64 (1).]

POSTULATE B2.  $ab \dashv a$  in  $T$  [By 66, 64 (1)]

POSTULATE B3.  $a \dashv aa$  in  $T$  [By 36, 65 (1), 64 (1).]

POSTULATE B4	$(ab)c \dashv a(bc)$ in $T$	[By 13, 65 (1), 64 (1)]
POSTULATE B5	$a \dashv a''$ in $T$ .	[By 31, 65 (1), 64 (1)]
POSTULATE B6	$[(a \dashv b)(b \dashv c) \dashv (a \dashv c)]$ in $T$ .	[By 16]
POSTULATE B7	$[a(a \dashv b) \dashv b]$ in $T$	[By 17]
POSTULATE B8	$a^* \dashv (ab)^*$ in $T$	[By 78, 64 (1)]
POSTULATE B9	$\exists (a, b) \cdot [(a \dashv b)'(a \dashv b')']$ not in $T$	[See Note 1]

*Note 1.* The existence postulate B9 in Lewis's list is not included among our postulates 1–17, since it is not required for the proofs of any of our theorems, and since there is a certain advantage in leaving "existence" questions open. It must be added to our list, however, if our system is to agree strictly with Lewis's. The form in which B9 is here given is the form now preferred by Professor Lewis, cf. §10, below.

*Note 2* Postulate B5 is redundant, since J. C. C. McKinsey has shown that it can be deduced from Df2, Df3, B1, B2, B3, B6 (Bull Amer Math Soc, vol 40, pp 425–427, 1934). See 93 1, below.

*Note 3* As to the form here given to Lewis's "consistency postulate" B8, a closer rendition of Lewis's B8 would be  $(ab)^* \dashv a^*$  in  $T$ . The two forms are equivalent by Lewis's theorem 12.44 (our 93 2, below).

*Note 4* Postulate B8, though a theorem in our system (with base  $K, T, \times, ', \equiv$ ), is an independent postulate in Lewis's list (with base  $K, T, \times, ', ^*$ ). Postulate B8 may be replaced, however, by the following equivalent form

POSTULATE B8a  $a^* = a \equiv Z$ ,

as is proved in 99, below.

All Lewis's postulates (except B9) are deducible from our list 1–17, as indicated in brackets after each item, above.

All our postulates 1–17 (including Definitions A–D) are deducible from Lewis's list (without using B9). This is established by the following theorems, 91–98,—several of which are not explicitly mentioned in Lewis's book.

For brevity, we first introduce the following definition (read:  $a$  implies  $b$ ).

90.0. DEFINITION  $a \leqslant b \Leftrightarrow a \dashv b$  in  $T$ ; (Our 62b)  
and then establish three lemmas, as follows

90.1. LEMMA 1.  $a \leqslant b \& b \leqslant a \rightarrow a = b$

Proof by the rules of Adjunction (Adj.) and Replacement (Repl.)

90 2. LEMMA 2  $a \leq ab \rightarrow a = ab$

Proof By Adj and Repl,  $a \leq ab \& ab \leq a \rightarrow a = ab$  But by B2,  $ab \leq a$  always holds Hence,  $a \leq ab \rightarrow a = ab$

90 3 LEMMA 3  $a \leq b \& b \leq c \rightarrow a \leq c$

Proof By Adj,  $a \leq b \& b \leq c \rightarrow (a \dashv b)(b \dashv c)$  in  $T$  By B6  $(a \dashv b)(b \dashv c) \dashv (a \dashv c)$  in  $T$ , whence by the Rule of Inference,  $(a \dashv b)(b \dashv c)$  in  $T \rightarrow (a \dashv c)$  in  $T$  Hence  $a \leq b \& b \leq c \rightarrow a \dashv c$  in  $T$

(A fourth and fifth lemma will be proved in 94 4, 94 5, below)

In the following deductions from Lewis's list, the theorems numbered from 91 to 96 depend only on Postulates B1-B6.

91 1  $a \leq a$ , that is,  $a \dashv a$  in  $T$

Proof By B3, B2,  $a \leq aa$  and  $aa \leq a$  Hence by 90 3,  $a \leq a$

91 2  $a = aa$

Proof By B2, B3,  $aa \leq a$  and  $a \leq aa$  Hence by 90 1,  $a = aa$

92 1  $ab = ba$

Proof By B1,  $ab \leq ba$  By B1,  $ba \leq ab$  Hence by 90 1,  $ab = ba$

92 2  $(ab)c = a(bc)$

Proof By B4,  $(cb)a \leq c(ba)$  By 92 1,  $(cb)a = (bc)a = a(bc)$

Hence,  $a(bc) \leq c(ba)$  By 92 1,  $c(ba) = (ba)c = (ab)c$

Hence,  $a(bc) \leq (ab)c$  But by B4,  $(ab)c \leq a(bc)$

Hence by 90 1,  $(ab)c = a(bc)$

93 1  $a'' = a$

Proof (after McKinsey) By Df2, 92 1,  $a' \dashv a' = (a'a'')^* = (a''a')^* = a'' \dashv a$  By 91 1,  $a' \dashv a'$  in  $T$  Hence,  $a'' \dashv a$  in  $T$  (1)

By (1),  $a''' \dashv a''$  in  $T$  Hence by 90 3, 90 0,  $a''' \dashv a$  in  $T$

By Df2, 92 1,  $a''' \dashv a = (a''''a')^* = (a''a'')^* = a' \dashv a''$

Hence,  $a' \dashv a''$  in  $T$  By (1),  $a''' \dashv a'$  in  $T$  Hence by 90 1,  $a''' = a'$

Hence, by Df2,  $a \dashv a'' = (aa'')^* = (aa')^* = a \dashv a$  By 91 1,  $a \dashv a$  in  $T$

Hence,  $a \dashv a''$  in  $T$  (2)

From (1) and (2), by 90 1,  $a'' = a$  (From this theorem, Postulate B5 follows as a corollary, by 91 1)

93 2  $a \dashv b = b' \dashv a'$

Proof By Df2, 92 1, 93.1,  $a \dashv b = (ab')^* = (b'a'')^* = b' \dashv a'$

94 1  $aa' = bb'$ , whence DEFINITION B  $Z = aa'$  (Not in the Lewis and Langford book)

**Proof** By Df2, 92,  $aa' \dashv c = [(aa')c']^* = [(ac')a']^* = ac' \dashv a$  By B2,  $ac' \dashv a$  in  $T$ . Hence,  $aa' \dashv c$  in  $T$ . Hence,  $aa' \dashv bb'$  in  $T$  and  $bb' \dashv aa'$  in  $T$ . Hence by 90 1,  $aa' = bb'$

94 2  $a \dashv a = Z^*$ , and  $Z^*$  in  $T$

**Proof** By B2, 94 1,  $a \dashv a = (aa')^* = Z^*$  By 91.1,  $a \dashv a$  in  $T$ . Hence,  $Z^*$  in  $T$

94 3  $aZ = Z$

**Proof** By 94 1, 92 2, 91.2,  $aZ = a(aa') = (aa)a' = aa' = Z$

94 4 **LEMMA 4**  $a \leq b \rightarrow ac \leq bc$

**Proof** By B6,  $(cd' \dashv b')(b' \dashv a') \dashv (cd' \dashv a')$  in  $T$  (1)

By Df2, 93 1, 92,  $(cd' \dashv b') = [(cd')b]^* = [(bc)d']^* = (bc \dashv d)$  (a)

By 93 2,  $b' \dashv a' = b \dashv a$  (b)

By Df2, 93 1, 92,  $(cd' \dashv a') = [(cd')a]^* = [(ac)d']^* = (ac \dashv d)$  (c)

From (a), (b), (c) in (1),  $(bc \dashv d)(a \dashv b) \dashv (ac \dashv d)$  in  $T$  (2)

Hence, putting  $bc$  for  $d$  and using 94 2,  $Z^*(a \dashv b) \dashv (ac \dashv bc)$  in  $T$

Hence, by Adjunction and Inference,

$Z^*$  in  $T$  &  $a \dashv b$  in  $T \rightarrow ac \dashv bc$  in  $T$

But by 94 2,  $Z^*$  in  $T$  holds Hence,  $a \dashv b$  in  $T \rightarrow ac \dashv bc$  in  $T$

94 5 **LEMMA 5**  $a \leq b \ \& \ a \leq c \rightarrow a \leq bc$

**Proof** By 94 4, 92.1, 90 3, 91 2,  $a \leq b \ \& \ a \leq c \rightarrow aa \leq ab \ \& \ ab \leq bc \rightarrow aa \leq bc \rightarrow a \leq bc$

94 6  $aZ' = a$  (Not in the book)

**Proof** By Df2, 93 1, 94 3,  $a \dashv Z' = (aZ'')^* = (aZ)^* = Z^*$  By 94 2,  $Z^*$  in  $T$ . Hence,  $a \dashv Z'$  in  $T$ , that is,  $a \leq Z'$ . Hence by 94 4,  $aa \leq aZ'$ , whence by 91 2,  $a \leq aZ'$ . Hence by 90 2,  $aZ' = a$

95 1  $a(ab)' = ab'$

**Proof** By Df2, 93 1, 92, 94 1,  $a(ab)' \dashv b' = [a(ab)'b]^* = [(ab)(ab)']^* = Z^*$ , whence by 94 2, 90 0,  $a(ab)' \leq b'$  Hence by 94 4, 91 2,  $a(ab)' \leq ab'$  (1)

By B2, 93 2,  $b' \leq (ab)'$  By B2, 92 1,  $ab' \leq b'$  Hence by 90 3,  $ab' \leq (ab)'$ . Hence by 94 4, 91.2,  $ab' \leq a(ab)'$  (2)

From (1), (2), by 90 1,  $a(ab)' = ab'$

95.2  $a \dashv b = a \dashv ab$

**Proof.** By Df2, 95 1,  $a \dashv b = (ab)^* = [a(ab)']^* = a \dashv ab$

95 3.  $a(a'b)' = a$

**Proof** By B2,  $a'b' \leq a'$ . Hence by 93 2, 93 1,  $a \leq (a'b')$ .  
 Hence by 94 4, 91 2,  $a \leq a(a'b')'$ . Hence by 90 2,  $a(a'b')' = a$ .

$$96.1 \quad (a'b')(a'b')' = a \quad (\text{Our 14})$$

**Proof** By B2, 93 2,  $a \leq (a'b)'$  and  $a \leq (a'b')'$ .

Hence by 94.5, 91 2,  $a \leq (a'b)(a'b)'$  (1)

By Df2, 95 1, 94.1,  $(a'b)(a'b)' + a = [(a'b)(a'b)' + a]^*$   
 $= [(a'b)(a'b)]^* = Z^*$ , whence by 94 2,  $(a'b)(a'b)' \leq a$  (2)

From (1), (2), by 90 1,  $(a'b)(a'b)' = a$

$$96.2 \quad a(b'c)' = [(ab)'(ac)']' \quad (\text{Proof as for our 39})$$

The next two theorems, 97 and 98, require the use of B8. That they cannot be proved from Lewis's list without the use of B8 is shown by Example B8, below.

$$97 \quad a \dashv b = ab \equiv a \quad (\text{Our 74.}) \quad (\text{Not in the book})$$

**Proof** (As indicated in the footnote at the beginning of this paper, the proof of 97 from Lewis's postulates follows as a corollary from my paper of 1934. For a valuable suggestion in connection with the following more direct proof, I am indebted to W. T. Parry.)

By B8,  $a^* \dashv (aa)^*$  in T. Hence by 94.1,  $a^* \leq Z^*$  (1)

By Df2,  $a \dashv ab = [a(ab)]^*$ , and by Df2, 92, 94 3,  $ab \dashv a = [aba']^* = Z^*$ . Hence by (1),  $a \dashv ab \leq ab \dashv a$ . Hence by 94.4, 91 2,  $a \dashv ab \leq (a \dashv ab)(ab \dashv a)$ , whence by 90 2,  $a \dashv ab = (a \dashv ab)(ab \dashv a)$ . Hence by 95 2, Df3,  $a \dashv b = ab \equiv a$ .

$$98 \quad a^* = a \equiv Z \quad (\text{Not in the book}) \quad (\text{Our Def C})$$

**Proof** By 91 2, 93 1, Df2, 97, 94.1,  
 $a^* = (aa'')^* = a \dashv a' = aa' \equiv a = Z \equiv a = a \equiv Z$

These theorems 91–98 show that all our Postulates 1–17, including Definitions A–D, are deducible as theorems from Lewis's list, without using B9. Thus the complete equivalence of our Postulates 1–17 and Lewis's Postulates B1–B8 is established.

The following Theorem 99 is added to show that Theorem 98 may be taken as a postulate in Lewis's system, in place of Postulate B8. Thus, if we adopt

**POSTULATE B8a**    $a^* = a \equiv Z$ , where  $Z = aa'$ ,  
 then B8 becomes a theorem, as follows

$$99 \quad a^* \dashv (ab)^* \text{ in T}$$

**Proof** (by B1–B6 and B8a). By Df2, 94.3,  $Z \dashv a = (Za')^* = Z^*$ .  
 Hence  $Z \dashv b' = Z \dashv a$ . By B8a, Df3,  $a^* = a \equiv Z = (a \dashv Z)(Z \dashv a)$ .

Hence  $a^* = (a \dashv Z)(Z \dashv b')$  By Df2, 93.1,  $(ab)^* = (a \dashv b')$

Hence  $a^* \dashv (ab)^* = (a \dashv Z)(Z \dashv b') \dashv (a \dashv b')$

Hence by B6,  $a^* \dashv (ab)^*$  in  $T$

Theorems 98 and 99 together show that Postulates B8 and B8a are interchangeable in Lewis's list.<sup>9</sup>

### §10 NOTE ON EXISTENCE POSTULATES

Lewis's existence postulate B9 is, in our notation

B9  $\exists (a, b) \{[(a \dashv b)'(a \dashv b')']' \text{ not in } T\}$

Another existence postulate which suggests itself as a possible addition to the list is

B10  $\exists a \{a \text{ not in } T \& a' \text{ not in } T\}$

[Here B9 is independent of B1-B8, B10, and B10 is independent of B1-B9, as is shown by Examples B9 and B10, below] The suggested postulate B10, while not technically included in Lewis's list, would appear to be entirely in keeping with the spirit of his theory.

*Note 1* The contradictory of B9, which we may call B9', is

B9'  $[(a \dashv b)'(a \dashv b')]' \text{ in } T$

<sup>9</sup> On page 151 of "Symbolic Logic," Lewis raises the question whether his theorems 19.6, 19.61, 19.62 can be proved from B1-B7, without the use of B8. Our examples B8a and B8 show that 19.6 and 19.62 cannot be so proved. The question in regard to 19.61 is still open. (It has been shown, however, by one of my students, Mr H. M. Syer, that if an "example" for 19.61 exists, it must contain at least sixteen elements.) For convenience of reference, we append direct proofs of these theorems, on the basis of B1-B8.

19.6.  $(a \dashv b) \dashv (ac \dashv bc)$  in  $T$

Proof. By Df2,  $a \dashv b = (ab')^*$  By B8,  $(ab')^* \dashv (acb')^*$ .

By 94.3, 94.6, 93.1, 96.2,

$(acb')^* = [(acb')'(acb')']^* = [(ac)(bc)]^* = ac \dashv bc$  Hence the theorem.

19.61.  $(a \dashv b)(a \dashv c) \dashv (a \dashv bc)$  in  $T$

Proof. By 19.6,  $(a \dashv b) \dashv (ac \dashv bc)$  in  $T$  Hence by 19.6, 95.2,

$(a \dashv b)(a \dashv c) \dashv (ac \dashv bc)(a \dashv ac)$  in  $T$  By 92.1, B6,

$(ac \dashv bc)(a \dashv ac) \dashv (a \dashv bc)$  in  $T$  Hence the theorem, by B6 and Inf.

19.62.  $(a \dashv bc) \dashv (a \dashv b)(a \dashv c)$  in  $T$

Proof. By B8,  $\{( (ab')'(ac')' )' \}^* \dashv \{ (ab')[(ab')'(ac')']' \}^*$  in  $T$ .

Hence by 96.2, 95.3,  $[(a(bc))']^* \dashv (ab')^*$  in  $T$  Hence by Df2,

$(a \dashv bc) \dashv (a \dashv b)$  in  $T$ , and by 92.1,  $(a \dashv bc) \dashv (a \dashv c)$  in  $T$

Hence the theorem, by Adj

The contradictory of B10, which we may call B10', is

$$\text{B10}' \quad a \text{ not in } T \rightarrow a' \text{ in } T$$

If we regard " $\dashv$ " for the moment as an undefined symbol, we observe that B9' is a characteristic formula of the Whitehead-Russell theory of "material implication", and that B10', while not technically a part of the theory of material implication, is entirely in keeping with the spirit of that theory (In fact, B10', in the form "Either  $a$  is in  $T$  or  $a'$  is in  $T$ ," is, in effect, a part of the "informal" presentation of the theory in *Principia Mathematica*)

*Note 2* A system  $(K, T, \times, ', *)$  which satisfies B1-B10 may or may not have its  $Z^*$  distinct from its  $Z'$ . If such a system does have its  $Z^*$  distinct from its  $Z'$ , then it must contain at least eight elements

*Note 3* Lewis's postulate B9 must not be confused with the following weaker postulate B11

$$\text{B11} \quad \exists (a, b) [(a \dashv b) \text{ not in } T \& (a \dashv b') \text{ not in } T]$$

This relation B11 is a consequence of B1-B8, and is therefore redundant

*Note 4* Lewis's postulate B9 must not be confused with the following stronger postulate F

$$\text{F} \quad \exists (a, b) [(a \dashv b)' \text{ in } T \& (a \dashv b')' \text{ in } T]$$

[Here F is independent of B1-B10. Also, B10 is independent of B1-B9 and F. But B9 is deducible from B1-B8 and F, so that F (in conjunction with B1-B8) is "stronger" than B9.] *This postulate F is not a part of Lewis's theory.* Also, the contradictory of F, namely

$$\text{F}' \quad (a \dashv b)' \text{ in } T \rightarrow (a \dashv b)' \text{ not in } T,$$

is not a characteristic formula of material implication, since it may coexist with B1-B10 (see Example F, below)

### §11 EXAMPLES FOR CONSISTENCY OF POSTULATES 1-17

The following examples of systems  $(K, T, \times, ', =)$  satisfy all the Postulates 1-17. Any one of these examples establishes the consistency of the postulates. The examples with eight and sixteen elements are included for reference, because they are rather troublesome to reproduce and exhibit very clearly the flexibility of the Lewis theory.

In the double-entry tables it is understood that  $a$  is in the left-hand margin, and  $b$  along the top

**EXAMPLE 01.**  $K =$  a class of four elements, denoted by 1, 2, 3, 4.  $T =$  the subclass of two elements, 1, 2.  $ab$ ,  $a'$ , and  $a \equiv b$  as in the accompanying tables (Tables for  $a^*$  and  $a \dashv b$  are added for reference, see Defs C, D)

$ab$	1 2 3 4	$a   a'$	$a \equiv b$	1 2 3 4	$a   a^*$	$a \dashv b$	1 2 3 4
1	1 2 3 4	1 4	1	2 4 4 4	1 4	1	2 4 4 4
2	2 2 4 4	2 3	2	4 2 4 4	2 4	2	2 2 4 4
3	3 4 3 4	3 2	3	4 4 2 4	3 4	3	2 4 2 4
4	4 4 4 4	4 1	4	4 4 4 2	4 2	4	2 2 2 2

Here  $Z = 4$ ,  $Z' = 1$ , and  $Z^* = 2$

**EXAMPLE 02**  $K, T, ab, a'$  as in Ex 01,  $a \equiv b$  as in table

$a \equiv b$	1 2 3 4	$a   a^*$	$a \dashv b$	1 2 3 4
1	1 4 3 4	1 4	1	4 3 4 4
2	4 1 4 3	2 3	2	1 1 3 3
3	3 4 1 4	3 4	3	1 4 1 4
4	4 3 4 1	4 1	4	1 1 1 1

Here  $Z = 4$ ,  $Z' = 1$ , but  $Z^* = 1$

**EXAMPLE 03**  $K, T, ab, a'$  as in Ex 01,  $a \equiv b$  as in table.

$a \equiv b$	1 2 3 4	$a   a^*$	$a \dashv b$	1 2 3 4
1	1 4 4 4	1 4	1	4 4 4 4
2	4 1 4 4	2 4	2	1 1 4 4
3	4 4 1 4	3 4	3	1 4 1 4
4	4 4 4 1	4 1	4	1 1 1 1

Here  $Z = 4$ ,  $Z' = 1$ ,  $Z^* = 1$

These three examples, taken from Lewis and Langford's Symbolic Logic, page 493, can easily be shown to be the only four-element systems which satisfy all the postulates 1-17 (except that in Examples 02 and 03, " $T = 1, 2$ " may be replaced by " $T = 1''$ ")

In all three of these examples, we have the following "relation-tables," in which a dot means "yes" and the absence of a dot means "no"

$a$ in $T$	$ab$ in $T$	$a'$ in $T$	$a \equiv b$ in $T$	$a^*$ in $T$	$a \dashv b$ in $T$
1	1 2 3 4		-	1 2 3 4	-
2		1	1	1	1
3	2	2	2	2	2
4	3	3	3	3	3
	4	4	4	4	4

**EXAMPLE 04.**  $K = 1, 2, 3, 4, 5, 6, 7, 8$ ,  $T = 1, 2$ , (W T Parry, Mind, vol 43, 1934)

$ab$	1	2	3	4	5	6	7	8	$a'$	$a^*$	$a \oplus b$	1	2	3	4	5	6	7	8	$a'$	$a^*$	$a \oplus b$	1	2	3	4	5	6	7	8
1	1	2	3	4	5	6	7	8	1	8	1	2	6	8	6	8	8	8	8	1	8	1	2	6	8	6	8	8	8	
2	2	2	4	4	6	6	8	8	2	7	2	6	9	8	8	8	8	8	8	2	8	2	2	2	8	8	8	8		
3	3	4	3	4	7	8	7	8	3	6	3	8	8	2	6	8	8	8	8	3	8	3	2	6	2	6	8	8	8	
4	4	4	4	4	8	8	8	8	4	5	4	8	8	6	2	8	8	8	8	4	8	4	2	2	2	2	8	8	8	
5	5	6	7	8	5	6	7	8	5	4	5	8	8	8	8	2	6	8	8	5	8	5	2	6	8	8	2	6	8	8
6	6	6	8	8	6	6	8	8	6	8	6	8	8	8	6	2	8	8	8	6	8	6	2	2	8	8	2	2	8	8
7	7	8	7	8	7	8	7	8	7	2	7	8	8	8	8	2	6	8	8	7	6	7	2	6	2	6	2	8	2	6
8	8	8	8	8	8	8	8	8	8	1	8	8	8	8	8	8	6	2	8	8	8	2	8	2	2	2	2	8	2	2

Here  $Z = 8$ ,  $Z' = 1$ ,  $Z^* = 2$ . Here A gives  $a = b$  when and only when  $a$  and  $b$  are the same. All the postulates 1-17 are found to be satisfied. (All except 13, 14, 16 require merely an inspection of the tables, 16 is verified by an examination of cases. The easiest way to verify 13 and 14 is by replacing the elements 1, 2, 3, 4, 5, 6, 7, 8 by the factors of Sheffer's "Boolean number" 30 in the following order 1, 2, 3, 6, 5, 10, 15, 30, and interpreting  $ab$  as the least common multiple of  $a$  and  $b$ , and  $a'$  as the quotient 30/a.) "Relation tables" are as follows.

$a$ in $T$	$a'$ in $T$	$a \oplus b$ in $T$	$a^*$ in $T$	$a \dashv b$ in $T$
-	-	-	-	-
1	1	1	1	1
2	2	2	2	2
3	3	3	3	3
4	4	4	4	4
-	-	-	-	-
5	5	5	5	5
6	6	6	6	6
7	7	7	7	7
8	8	8	8	8

EXAMPLE 05  $K = 1, 2, 3, 4, 5, 6, 7, 8$ .  $T = 1, 2$

$ab$  and  $a'$  as in Ex. 04, and  $a \oplus b$  as in the following new table.

$a \oplus b$	1	2	3	4	5	6	7	8	$a$	$a^*$	$a \dashv b$	1	2	3	4	5	6	7	8
1	2	4	8	8	6	8	8	8	1	8	1	2	4	8	8	6	8	8	8
2	4	2	8	8	8	6	8	8	2	8	2	2	2	8	8	6	8	8	8
3	8	8	2	4	8	8	8	8	3	8	3	2	4	2	4	6	8	6	8
4	8	8	4	2	8	8	8	6	4	6	4	2	2	2	2	6	6	6	6
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	6	8	8	8	2	4	8	8	5	8	5	2	4	8	8	2	4	8	8
6	8	6	8	8	4	2	8	8	6	8	6	2	2	8	8	2	2	8	8
7	8	8	6	8	8	2	4	2	7	4	7	2	4	2	4	2	4	2	4
8	8	8	8	6	8	8	4	2	8	2	8	8	3	3	2	2	2	2	2

Here  $Z = 8$ ,  $Z' = 1$ ,  $Z^* = 2$ , as in Ex. 04. All the postulates 1-17 are satisfied. In spite of the greater variety in the table for  $a^*$ , the "relation tables" for this example are exactly the same as those for Ex. 04.

**EXAMPLE 0.6.** This example contains sixteen elements, and exhibits more clearly than any smaller one can do the characteristic flexibility of the system of strict implication. In particular, the subclass  $T$  contains other elements besides  $Z'$  and  $Z^*$ , and there are many elements which belong neither to  $T$  nor to  $T'$  (see 53). The basic symbols ( $K$ ,  $T$ ,  $\times$ ,  $'$ ,  $\equiv$ ) are specified as follows

$$K = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16$$

$$T = 1, 2, 3, 4$$

(In the tables, the places which the zero element 16 should occupy are left blank, in order to exhibit more clearly to the eye the "pattern" of the system.)

$ab$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	$a'$
1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15		1
2	2	2	4	4	6	6	8	8	10	10	12	12	14	14			2
3	3	4	3	4	7	8	7	8	11	12	11	12	15	15			3
4	4	4	4	4	8	8	8	8	12	12	12	12					4
5																	
6	5	6	7	8	5	6	7	8	13	14	15		13	14	15		5
7	6	6	8	8	6	6	8	8	14	14			14	14			6
8	7	8	7	8	7	8	7	8	15	15			15	15			7
9	8	8	8	8	8	8	8	8									8
10																	
11	9	10	11	12	13	14	15	16	9	10	11	12	13	14	15		9
12	10	10	12	12	14	14			10	10	12	12	14	14			10
13	11	12	11	12	15	15			11	12	11	12	15	15			11
14	12	12	12	12					12	12	12	12					12
15																	
16	13	14	15		13	14	15		13	14	15		13	14	15		13
	14	14			14	14			14	14			14	14			14
	15	15			15	15			15	15			15	15			15
	16																16

$a \equiv b$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	$a'$
1	4	8			8	8			12								
2	8	4			8	8				12							
3		4	8		8	8				12							
4		8	4		8	8					12						
5	8	8			4	8						12					
6	8	8			8	4							12				
7		8	8		4	8							12				
8		8	8		8	4								12			
9	12								4	8			8	8			
10		12							8	4			8	8			
11		12								4	8		8	8			
12			12							8	4		8	8			
13				12					8	8			4	8			
14					12				8	8			8	4			
15						12				8	8		8	8		4	
16							12			8	8		8	8		8	4

The tables for  $a^*$  and  $a \cdot b$ , by Defs. C and D, are as follows

$a$	$a^*$	$a \cdot b$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	16		1	4	8		8	8			12							
2	16		2	4	4		8	8			12	12						
3	16		3	4	8	4	8	8	8	8	12	12						
4	16		4	4	4	4	4	8	8	8	12	12	12	12				
5	16		5	4	8		4	8			12			12				
6	16		6	4	4		4	4			12	12		12	12			
7	16		7	4	8	4	8	4	8	8	12	12	12	12	12	12	12	
8	12		8	4	4	4	4	4	4	4	12	12	12	12	12	12	12	
9	16		9	4	8		8	8			4	8		8	8			
10	16		10	4	4		8	8			4	4		8	8			
11	8		11	4	8	4	8	8	8	8	4	8	4	8	8	8	8	
12	8		12	4	4	4	4	8	8	8	4	4	4	4	8	8	8	
13	16		13	4	8		4	8			4	8		4	8			
14	16		14	4	4		4	4			4	4		4	4			
15	8		15	4	8	4	8	4	8	4	8	4	8	4	8	4	8	
16	4		16	4	4	4	4	4	4	4	4	4	4	4	4	4	4	

Here  $Z = 16$ ,  $Z' = 1$ , and  $Z^* = 4$ . All the postulates 1-17 are found to be satisfied (Postulate 16 is verified by a somewhat laborious examination of cases. Postulates 13 and 14 are most easily verified by replacing the elements 1, 2, ..., 16 by the factors of the Boolean number 210 in the following order

1, 2, 3, 6, 5, 10, 15, 30, 7, 14, 21, 42, 35, 70, 105, 210,

and interpreting  $ab$  as the least common multiple of  $a$  and  $b$ , and  $a'$  as the quotient  $210/a$ . The relation " $a \cdot b$  in  $T$ " then means " $a$  contains  $b$  as a factor")

The relation tables for  $a$  in  $T$ ,  $a'$  in  $T$ ,  $a \equiv b$  in  $T$ , and  $a \cdot b$  in  $T$  may be readily constructed by the reader.

## §12 EXAMPLES FOR INDEPENDENCE

### §12a. EXAMPLES 1-4

Each of the following examples of systems  $(K, T, \times, ', \equiv)$  violates the postulate with corresponding number

EXAMPLE 1  $K = 1, 2$   $T = 1$

$ab$	1	2	$a$	$a'$	$a \equiv b$	1	2
—	—	—	—	—	—	—	—
1	1	w	1	2	1	1	2
w	2	3	w	1	2	2	1

Here 1 fails 2, 3, 4, 5, 6, hold. Def A gives  $1 = 1, 2 = 2$ , so that 7-14 hold in so far as the elements involved are in  $K$ .

**EXAMPLE 2**  $K = 1, 2 \quad T = 1$

$$\begin{array}{c|cc} ab & 1 & 2 \\ \hline - & - & - \\ 1 & 1 & 2 \\ 2 & 2 & 2 \end{array} \qquad \begin{array}{c|c} a & a' \\ \hline - & - \\ 1 & 2 \\ 2 & w \end{array} \qquad \begin{array}{c|cc} a \equiv b & 1 & 2 \\ \hline - & - & - \\ 1 & 1 & 2 \\ 2 & 2 & 1 \end{array}$$

Here 2 fails 1, 3, 4, 5, 6, hold Def A gives  $1 = 1, 2 = 2$ , so that 7-14 hold in so far as the elements involved are in  $K$

**EXAMPLE 3**  $K = 1, 2 \quad T = 1$

$$\begin{array}{c|cc} ab & 1 & 2 \\ \hline - & - & - \\ 1 & 1 & 2 \\ 2 & 2 & 2 \end{array} \qquad \begin{array}{c|c} a & a' \\ \hline - & - \\ 1 & 2 \\ 2 & 1 \end{array} \qquad \begin{array}{c|cc} a \equiv b & 1 & 2 \\ \hline - & - & - \\ 1 & 1 & w \\ 2 & w & 1 \end{array}$$

Here 3 fails 1, 2, 4, 5, 6 hold Def A gives  $1 = 1, 2 = 2$ , so that 7-14 hold in so far as the elements involved are in  $K$

**EXAMPLE 4a**  $K = 1, 2 \quad T = 1, 3$

$$\begin{array}{c|cc} ab & 1 & 2 \\ \hline - & - & - \\ 1 & 1 & 2 \\ 2 & 2 & 2 \end{array} \qquad \begin{array}{c|c} a & a' \\ \hline - & - \\ 1 & 2 \\ 2 & 1 \end{array} \qquad \begin{array}{c|cc} a \equiv b & 1 & 2 \\ \hline - & - & - \\ 1 & 1 & 2 \\ 2 & 2 & 1 \end{array}$$

Here 4a fails, since the element 3 is in  $T$  and not in  $K$  1, 2, 3, 4b, 4c, hold 5-14 hold in so far as the elements involved are in  $K$  (The verification of 13 and 14 is accomplished by a simple examination of cases )

**EXAMPLE 4b**  $K = 1, 2 \quad T = \text{an empty class}$   
 $ab, a', a \equiv b$  as in Ex 4a

Here 4b fails 1, 2, 3, hold 4a holds (vacuously) 4c holds 5, 6 hold (vacuously) Def A gives  $a = b$  never true, so that 7-10 hold vacuously 11-14 fail As noted above, if any one of the postulates 11-14 is included, 4b may be replaced by the weaker form  $\exists a$  ( $a$  in  $K$ )

**EXAMPLE 4c**  $K = 1, 2 \quad T = 1, 2 \quad ab, a', a \equiv b$  as in Ex 4a

Here 4c fails. 1, 2, 3, 4a, 4b, 5, 6 hold Def A gives  $a = b$  true for all values, so that 7-14 hold

These six examples show that Postulates 1, 2, 3, 4a, 4b, 4c are independent of each other With the exception noted under 4b, they are also independent of 5-14

### §12b EXAMPLES 5-14

**EXAMPLE 5**  $K = 1, 2, 3, 4, 5, 6, 7, 8 \quad T = 1, 2, 3, 4, 5, 6$   
 $ab$  and  $a'$  as in Example 0.4 (Boolean algebra),  $a \oplus b$  as in table

$a \oplus b$	1	2	3	4	5	6	7	8
$a$	$a^*$							
1	1	2	3	8	8	8	8	8
2	2	1	8	8	8	8	8	8
3	8	8	1	2	8	8	8	8
4	8	8	2	1	8	8	8	8
5	8	8	8	8	1	2	8	8
6	8	8	8	8	2	1	8	8
7	8	8	8	8	8	1	2	8
8	8	8	8	8	2	1	8	8

Here  $Z = 8$ ,  $Z^* = 1$ . Postulate 5 fails, since 5 and 4 are in  $T$ , while  $5 \times 4 [= 8]$  is not in  $T$ . Postulates 1-4, 6-14 all hold. (By A, we have not only  $1 = 1, 2 = 2, \dots, 8 = 8$ , but also  $1 = 2, 3 = 4, 5 = 6$ , and  $7 = 8$ .)

EXAMPLE 6  $K = 1, 2, 3, 4$      $T = 2$   
 $ab, a', a \oplus b$  as in Example 01    ( $Z = 4, Z^* = 2$ )

Here 6 fails, since  $1 \times 2 [= 2]$  is in  $T$ , while 1 is not in  $T$  Postulates 1-5, 7-14 hold

**EXAMPLE 7**  $K = 1, 2, 3, 4 \quad T = 1, 2$   
 $ab$  and  $a'$  as in Example 0 1    $a \equiv b$  as in table   ( $Z = 4, Z^* = 1$ )

$a \oplus b$	1	2	3	4
1	1	1	1	1
2	1	1	2	1
3	1	2	1	1
4	1	1	1	1

Here 7 fails, since 2 is in  $T$  and  $2 \equiv 4 \pmod{1}$  is in  $T$ , while 4 is not in  $T$ . Postulates 1-6, 8-14 hold (By A, we have  $a = b$  for all values of  $a$  and  $b$ .)

**EXAMPLE 8**  $K = 1, 2, 3, 4, 5, 6, 7, 8 \quad T = 1, 2$   
 $ab$  and  $a'$  as in Example 04    $a \cdot b$  as in table   ( $Z = 8, Z^* = 1$ )

a	b	1	2	3	4	5	6	7	8
1	1	2	6	8	8	8	8	8	8
2	2	1	4	8	8	8	8	8	8
3	8	8	1	8	8	8	8	8	8
4	8	8	8	1	8	8	8	8	8
5	8	8	8	6	1	8	8	8	8
6	8	8	8	8	8	1	8	8	8
7	8	8	8	8	8	8	1	2	1
8	8	8	8	8	8	8	2	1	1

Here 8 fails, since  $1 \equiv 2 [= 2]$  is in  $T$ , while  $1 \times 5 \equiv 2 \times 5 [= 8]$  is not in  $T$ . Postulates 1-7, 9-14 hold (By A, we have not only  $1 = 1$ ,  $2 = 2$ ,  $8 = 8$ , but also  $1 = 2$  and  $7 = 8$ )

**EXAMPLE 9**  $K = 1, 2, 3, 4, 5, 6, 7, 8 \quad T = 1, 2$   
 $ab$  and  $a'$  as in Example 0.4  $a \equiv b$  as in table ( $Z = 8$ ,  $Z^* = 1$ )

$a \equiv b$	1	2	3	4	5	6	7	8
1	1	2	8	8	8	8	8	8
2	2	1	8	8	8	8	8	8
3	8	8	1	2	8	8	8	8
4	8	8	2	1	8	8	8	8
-								
5	8	8	8	8	1	2	2	2
6	8	8	8	8	2	1	2	2
7	8	8	8	8	2	2	1	2
8	8	8	8	8	2	2	2	1

Here 9 fails, since  $5 \equiv 7$  is in  $T$ , while  $5' \equiv 7' [= 8]$  is not in  $T$  By A, we have not only  $1 = 1$ ,  $2 = 2$ ,  $8 = 8$ , but also  $1 = 2$ ,  $3 = 4$ ,  $5 = 6$ ,  $5 = 7$ ,  $5 = 8$ ,  $6 = 7$ ,  $6 = 8$ ,  $7 = 8$  Postulates 1-8, 10-14, hold

**EXAMPLE 10**  $K = 1, 2, 3, 4, 5, 6, 7, 8 \quad T = 1, 2$   
 $ab$  and  $a'$  as in Example 0.4  $a \equiv b$  as in table

$a \equiv b$	1	2	3	4	5	6	7	8
1	1	2	8	8	8	8	8	8
2	2	1	8	8	8	8	8	8
3	8	8	1	2	8	8	8	8
4	8	8	2	1	8	8	8	8
-								
5	8	8	8	8	1	2	6	8
6	8	8	8	8	2	1	8	8
7	8	8	8	8	6	8	1	2
8	8	8	8	8	8	8	2	1

Here 10 fails, since  $5 \equiv 6 [= 1]$  is in  $T$ , while  $(5 \equiv 7) \equiv (6 \equiv 7) [= 8]$  is not in  $T$  By A we have not only  $1 = 1$ ,  $2 = 2$ ,  $8 = 8$ , but also  $1 = 2$ ,  $3 = 4$ ,  $5 = 6$ ,  $7 = 8$  Postulates 1-9, 11-14 hold

**EXAMPLE 11**  $K = 1, 2, 3, 4. \quad T = 1, 2$   
 $ab$  and  $a'$  as in Example 0.1  $a \equiv b$  as in table

$a \equiv b$	1	2	3	4
1	2	4	4	4
2	4	3	4	4
3	4	4	2	4
4	4	4	3	2

Here 11 fails, since  $(3 \equiv 4) \equiv (4 \equiv 3) [= 3]$  is not in  $T$ . Postulates 1-10, 12-14 hold.

**EXAMPLE 12**  $K = 1, 2, 3, 4 \quad T = 1$   
 $ab, a'$ , and  $a \equiv b$  as in tables

$ab$	1 2 3 4	$a$	$a'$	$a \equiv b$	1 2 3 4
1	1 1 1 1	1	4	1	1 4 4 4
2	2 2 2 2	2	3	2	4 1 4 4
3	3 3 3 3	3	2	3	4 4 1 4
4	4 4 4 4	4	1	4	4 4 4 1

Here 12 fails, since  $(3 \times 4) \equiv (4 \times 3) [= 4]$  is not in  $T$ . Postulates 1-11, 13-14 hold. In this system the theorem  $aa' = bb'$  does not hold, and no zero-element  $Z$  exists.

**EXAMPLE 13**  $K = 1, 2, 3, 4 \quad T = 1 \quad ab, a', a \equiv b$  as in tables

$ab$	1 2 3 4	$a$	$a'$	$a \equiv b$	1 2 3 4
1	1 3 2 4	1	4	1	1 4 4 4
2	3 3 4 4	2	3	2	4 1 4 4
3	2 4 2 4	3	2	3	4 4 1 4
4	4 4 4 4	4	1	4	4 4 4 1

Here 13 fails, since  $(1 \times 2) \times 2 \equiv 1 \times (2 \times 2) [= 4]$  is not in  $T$ . Postulates 1-12 hold. Postulate 14 holds (by examination of cases).

**EXAMPLE 14**  $K = 1, 2, 3, 4 \quad T = 1, 2 \quad ab, a', a \equiv b$  as in tables

$ab$	1 2 3 4	$a$	$a'$	$a \equiv b$	1 2 3 4
1	1 2 4 4	1	4	1	2 4 4 4
2	2 2 4 4	2	3	2	4 2 4 4
3	3 4 4 4	3	2	3	4 4 2 4
4	4 4 4 4	4	1	4	4 4 4 2

Here 14 fails, since  $(2'3)' (2'3)' \equiv 2 [= 4]$  is not in  $T$ . Postulates 1-13 hold (13 by examination of cases).

These Examples 5-14 show that Postulates 5-14 are independent of Postulates 1-4 and of each other.

### §12c EXAMPLES 15-17.

**EXAMPLE 15**  $K = 1, 2, 3, 4 \quad T = 1, 2$   
 $ab$  and  $a'$  as in Example 01  $a \equiv b$  as in table  $(Z = 4, Z^* = 2)$

$a \equiv b$	1 2 3 4	$a$	$a^*$	$a \equiv b$	1 2 3 4	$a(a \equiv b)$	1 2 3 4	$ab \equiv a$	1 2 3 4
1	1 4 4 4	1	4	1	2 4 3 4	1	2 4 3 4	1	1 4 3 4
2	4 1 4 3	2	4	2	2 2 3 3	2	2 2 4 4	2	1 1 3 3
3	3 4 2 4	3	4	3	2 4 2 4	3	4 4 4 4	3	2 4 2 4
4	4 3 4 2	4	2	4	2 2 2 2	4	4 4 4 4	4	2 2 2 2

Here 15 fails, since  $(1 \equiv 3) (3 \equiv 1) \equiv (1 \equiv 3) = (3)(2) \equiv 3 = 4 \equiv 3 = 4$ , which is not in  $T$ . Postulates 1-6 hold. Definition A gives  $a = b$ .

when and only when  $a$  and  $b$  are the same Postulates 7-14 hold 16 holds, by examination of cases 17 holds, by inspection of the table for  $a(a+b)$  Hence 15 cannot be deduced from the other postulates of the list 1-17

We note also that Theorems 71-75, 78, and 87 fail, hence none of these theorems can be deduced from the postulates 1-17 if 15 is omitted

By way of parenthesis, the following alternative examples, 15a, 15b, may be of interest

EXAMPLE 15a  $K = 1, 2, 3, 4 \quad T = 1, 2$ .

$ab$  and  $a'$  as in Example 0 1  $a \equiv b$  as in table ( $Z = 4, Z^* = 2$ )

$a \equiv b$	1	2	3	4	$a$	$a^*$	$a \dashv b$	1	2	3	4	$a(a \dashv b)$	1	2	3	4	$ab \equiv a$	1	2	3	4
1	2	4	4	4	1	4	1	2	4	4	4	1	2	4	4	4	1	2	4	4	
2	4	2	3	4	2	4	2	2	2	4	4	2	2	2	4	4	2	2	2	4	
3	4	3	2	4	3	4	3	2	4	2	4	3	4	4	4	4	3	2	4	2	
4	4	4	4	2	4	2	4	2	2	2	2	4	4	4	4	4	4	2	2	2	

Here 15 fails, since  $(3 \dashv 2)(2 \dashv 3) \equiv (3 \equiv 2) = (4)(4) \equiv 3 = 4$ , which is not in  $T$  Postulates 7-14 hold 16 holds [by examination of cases] 17 holds [by inspection of table for  $a(a \dashv b)$ ] Also, all the theorems of §7 and §8 are satisfied Hence 15 cannot be proved from postulates 1-14, 16-17, even with the aid of §7 and §8

We note also that a theorem which we may call 15a  $(ab \equiv a)(ba \equiv b) = (a \equiv b)$  fails [when  $a = 2, b = 3$ ] Hence 15a cannot be proved from Postulates 1-14, 16-17, even with the aid of §7 and §8

EXAMPLE 15b  $K = 1, 2, 3, 4 \quad T = 1, 2$

$ab$  and  $a'$  as in Example 0 1  $a \equiv b$  as in table ( $Z = 4, Z^* = 1$ )

$a \equiv b$	1	2	3	4	$a$	$a^*$	$a \dashv b$	1	2	3	4	$a(a \dashv b)$	1	2	3	4	$ab \equiv a$	1	2	3	4
1	1	4	4	4	1	4	1	1	4	3	4	1	1	4	3	4	1	1	4	4	
2	4	1	4	3	2	3	2	1	1	3	3	2	2	2	4	4	2	1	1	3	
3	4	4	1	4	3	4	3	1	4	1	4	3	4	3	4	1	3	1	4	1	
4	4	3	4	1	4	1	4	1	1	1	1	4	4	4	4	4	4	1	1	1	

Here 15 fails, since  $(1 \dashv 3)(3 \dashv 1) \equiv (1 \equiv 3) = 4$ , which is not in  $T$  Postulates 7-14 hold 16 holds [by examination of cases] 17 holds [by inspection of table for  $a(a \dashv b)$ ] Also, a theorem which we may call 15a  $(ab \equiv a)(bu \equiv b) = (a \equiv b)$  holds [by inspection of table for  $ab \equiv a$ ] Hence 15 cannot be proved from Postulates 1-14, 16-17, even with the aid of 15a

We note also that Theorem 74 fails [when  $a = 1$  and  $b = 3$ ], while all the other theorems of §7 and §8 hold Hence 74 cannot be proved from Postulates 1-14, 16-17, even with the aid of all the other theorems of §7 and §8, and 15a

**EXAMPLE 16**  $K = 1, 2, 3, 4, 5, 6, 7, 8$ .  $T = 1, 2$   
 $ab$  and  $a'$  as in Example 04.  $a \equiv b$  as in table ( $Z = 8, Z^* = 2$ )

$a \equiv b$	1	2	3	4	5	6	7	8	$a$	$a^*$	$a \dashv b$	1	2	3	4	5	6	7	8
1	2	6	8	4	8	8	8	8	1	8	1	2	6	8	4	8	8	8	8
2	6	2	8	8	8	8	8	8	2	8	2	2	2	8	8	8	8	8	8
3	8	8	2	6	8	8	8	8	3	8	3	2	6	3	6	8	8	8	8
4	4	8	6	2	8	8	8	8	4	8	4	2	2	2	2	8	8	8	8
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	8	8	8	8	2	6	8	4	5	4	5	2	6	8	4	2	6	8	4
6	8	8	8	8	6	2	8	8	6	8	6	2	2	8	8	2	2	8	8
7	8	8	8	8	8	8	2	6	7	6	7	2	6	2	6	2	6	2	6
8	8	8	8	8	4	8	6	2	8	2	8	2	2	2	2	2	2	2	2

Here 16 fails, since  $(3+1)(1+4) \dashv (3+4) = (2)(4) \dashv 6 = 4 \dashv 6 = 8$ , which is not in  $T$ . Postulates 1-14 hold. 15 holds [by inspection of table for  $(a \dashv b)(b \dashv a)$ ]. 17 holds [by inspection of table for  $a(a \dashv b)$ ]. Hence, 16 cannot be deduced from 1-15, 17.

We note also that Theorem 78 fails, since  $5^* \dashv (5 \dashv 2) = 4 \dashv 6 = 8$ , which is not in  $T$ . Hence, 78 cannot be deduced from Postulates 1-17 if 16 is omitted.

The following alternative example, 16a, may also be of interest.

**EXAMPLE 16a**  $K = 1, 2, 3, 4, 5, 6, 7, 8$ .  $T = 1, 2$ .  
 $ab$  and  $a'$  as in Example 04.  $a \equiv b$  as in table ( $Z = 8, Z^* = 2$ )

$a \equiv b$	1	2	3	4	5	6	7	8	$a$	$a^*$	$a \dashv b$	1	2	3	4	5	6	7	8
1	2	4	4	8	8	8	8	8	1	8	1	2	4	4	8	8	8	8	8
2	4	2	4	4	8	8	8	8	2	8	2	2	4	4	8	8	8	8	8
3	4	4	2	4	8	8	8	8	3	8	3	2	4	2	4	8	8	8	8
4	8	4	4	2	8	8	8	8	4	8	4	2	2	2	2	8	8	8	8
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	8	8	8	8	2	4	4	8	5	8	5	2	4	4	8	2	4	4	8
6	8	8	8	8	4	2	4	4	6	4	6	2	2	4	4	2	2	4	4
7	8	8	8	8	4	4	2	4	7	4	7	2	4	2	4	2	4	2	4
8	8	8	8	8	8	4	4	2	8	2	8	2	2	2	2	2	2	2	2

Here 16 fails, since  $(5 \dashv 7)(7 \dashv 8) \dashv (5 \dashv 8) = (4)(4) \dashv 8 = 4 \dashv 8 = 8$ , which is not in  $T$ . Postulates 1-14 hold. 15 holds [by inspection of tables for  $a \dashv b$  and  $b \dashv a$ ]. 17 holds [by inspection of table for  $a(a \dashv b)$ ]. Also, Theorems 71-75, 78, 81-87 hold. Hence, Postulate 16 cannot be deduced from 1-15, 17, even with the aid of §7 and §8.

**EXAMPLE 17**  $K = 1, 2, 3, 4$ .  $T = 1, 2$ .  
 $ab$  and  $a'$  as in Example 01.  $a \equiv b$  as in table ( $Z = 4, Z^* = 1$ )

$a \equiv b$	1	2	3	4	$a$	$a^*$	$a \dashv b$	1	2	3	4
1	1	3	3	3	1	8	1	1	3	3	3
2	3	1	3	3	2	8	2	1	1	3	3
3	2	3	1	3	3	8	3	1	3	1	3
4	3	3	3	1	4	1	4	1	1	1	1

Here 17 fails, since  $3(3 \dashv 4) \dashv 4 = .(3)(3) \dashv 4 = 3 \dashv 4 = 3$ , which is not in  $T$ . Postulates 1-14 hold. 15 holds [by inspection of tables for  $a \dashv b$  and  $b \dashv a$ ]. 16 holds [by examination of cases]. Also, Theorems 71-75, 78 hold. Hence, 17 cannot be proved from 1-16, even with the aid of §7.

We note also that 81-87 fail. Hence, 81-87 cannot be deduced from Postulates 1-16 without the aid of 17.

### §12d EXAMPLES FOR B8 IN LEWIS'S LIST (SEE §9)

**EXAMPLE B8** Base  $(K, T, \times, ', *)$   $K = 1, 2, 3, 4, 5, 6, 7, 8$   
 $T = 1, 2$   $ab$  as in table,  $a'$  as in table,  $a^*$  as in table

$ab$	1	2	3	4	5	6	7	8	$a$	$a'$	$a$	$a^*$
1	1	2	3	4	5	6	7	8	1	8	1	8
2	2	2	4	4	6	6	8	8	2	7	2	8
3	3	4	3	4	7	8	7	8	3	6	3	8
4	4	4	4	4	8	8	8	8	4	5	4	8
5	5	6	7	8	5	6	7	8	5	4	5	8
6	6	6	8	8	6	6	8	8	6	3	6	3
7	7	8	7	8	7	8	7	8	7	2	7	8
8	8	8	8	8	8	8	8	8	8	1	8	2

Here  $Z = aa' = 8$ ,  $Z^* = 2$ .

In accordance with Definitions Df2 and Df3, we have the following tables for  $a \dashv b$  and  $a \equiv b$ .

$a \dashv b$	1	2	3	4	5	6	7	8	$a \equiv b$	1	2	3	4	5	6	7	8
1	2	8	3	8	6	8	8	8	1	2	8	4	8	8	8	8	8
2	2	2	3	8	8	8	8	8	2	8	2	8	4	8	8	8	8
3	2	8	2	8	8	8	8	8	3	4	8	2	8	8	8	8	8
4	2	2	2	8	8	8	8	8	4	8	4	8	2	8	8	8	8
5	2	8	3	8	2	8	3	8	5	8	8	8	8	2	8	4	8
6	2	2	3	8	2	2	3	8	6	8	8	8	8	8	2	8	4
7	2	8	2	8	2	8	2	8	7	8	8	8	8	4	8	2	8
8	2	2	2	8	2	2	2	2	8	8	8	8	8	8	4	8	2

In this example, B8 and B8a fail. [Take  $a = 6$  and  $b = 7$ .] All the other postulates of Lewis's list are found to be satisfied. [In verifying B4, note that  $(ab)c = a(bc)$  as in the example of a Boolean algebra in Example 0.4. B6 is verified by an examination of cases; B7 by inspection of a table for  $a(a \dashv b)$ . B9 is satisfied by the pair of elements  $a = 1, b = 7$ .] Note, however, that 97 and 98 fail, which shows that 97 and 98 cannot be deduced from B1-B7 without the use of B8 (or B8a). We note further that B10 holds, and that F holds ( $a = 3, b = 2$ ). Also, 19.62 fails (see footnote 9, above).

EXAMPLE B8a  $K, T, \times, ', \equiv$ , as in Example B8, with  $a^*$  given as follows  $4^* = 7, 8^* = 2$ , otherwise,  $a^* = 8$

In this example, B8 and B8a fail, B1-B7 and B9 hold, and B10 fails (see footnote 9, above)

### §12e EXAMPLES B9, B10, AND F (SEE §10)

EXAMPLE B9  $K = 1, 2, 3, 4, 5, 6, 7, 8 \quad T = 1$

$ab$	1	2	3	4	5	6	7	8	$a a$
1	1	2	3	4	5	6	7	8	1 8
2	2	2	4	4	6	6	8	8	2 7
3	3	4	3	4	7	8	7	8	3 6
4	4	4	4	4	8	8	8	8	4 5
5	5	6	7	8	5	6	7	8	5 4
6	6	6	8	8	6	6	8	8	6 3
7	7	8	7	8	7	8	7	8	7 2
8	8	8	8	8	8	8	8	8	8 1

$a \equiv b$	1	2	3	4	5	6	7	8	$a a^*$	$a \dashv b$	1	2	3	4	5	6	7	8
1	1	2	3	4	5	6	7	8	1 8	1	1	2	3	4	5	6	7	8
2	2	1	4	3	6	5	8	7	2 7	2	1	1	3	3	5	5	7	7
3	3	4	1	2	7	8	5	6	3 6	3	1	2	1	2	5	6	5	6
4	4	3	2	1	8	7	6	5	4 5	4	1	1	1	1	5	5	5	5
5	5	6	7	8	1	2	3	4	- -	5	1	2	3	4	1	2	3	4
6	6	5	8	7	2	1	4	3	6 3	6	1	1	3	3	1	1	4	4
7	7	8	5	0	3	4	1	2	7 2	7	1	2	1	2	1	2	1	2
8	8	7	6	5	4	3	2	1	8 1	8	1	1	1	1	1	1	1	1

Here B9 fails, since it will be found that  $[(a \dashv b)'(a \dashv b')']'$  is in  $T$  for all values of  $a$  and  $b$ . Postulates 1-17 hold. (15 by inspection, 16 by examination of cases, 17 by inspection), so that B1-B8 also hold. Hence B9 is independent of 1-17, and of B1-B8. (We note that B10 also holds, so that B9 cannot be deduced from B1-B8 even with the aid of B10. On the other hand, F of course fails.)

Since  $a^* = a'$ , this example is technically an example (in our notation) of a system of material implication. Note, however, that while the formal postulate B9' is satisfied, the "informal" postulate B10' is not satisfied in this example.

EXAMPLE B10  $K, T, \times, ', \equiv, ^*$ , the same as in Example 04, except that  $T = 1, 2, 3, 4$  instead of  $T = 1, 2$ .

Here B10 clearly fails. Postulates 1-17 and B1-B9 all hold. Hence B10 is independent of 1-17 and of B1-B9.

(We note that F also holds, taking  $a = 2, b = 3$ , so that B10 cannot be deduced from B1-B9 even with the aid of F.)

**EXAMPLE F**  $K = 1, 2, 3, 4, 5, 6, 7, 8 \quad T = 1, 2 \quad ab$  and  $a'$  as in Example B9  $a \equiv b$  and  $a^*$  and  $a \dashv b$  as in the following tables.

$a \equiv b$	1	2	3	4	5	6	7	8	$a$	$a^*$	$a \dashv b$	1	2	3	4	5	6	7	8
1	2	4	4	4	6	8	8	8	1	8	1	2	4	4	4	6	8	8	8
2	4	2	4	4	8	8	8	8	2	8	2	2	2	4	4	6	6	8	8
3	4	4	2	4	8	8	6	8	3	8	3	2	4	2	4	6	8	8	8
4	4	4	4	2	8	8	8	6	4	6	4	2	2	2	2	6	6	6	6
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5	6	8	8	8	2	4	4	4	5	4	5	2	4	4	4	2	4	4	4
6	8	6	8	8	4	2	4	4	6	4	6	2	2	4	4	2	2	4	4
7	8	8	6	8	4	4	2	4	7	4	7	2	4	2	4	2	4	2	4
8	8	8	6	4	4	4	2	2	8	2	8	2	2	2	2	2	2	2	2

Here F fails, since  $(a \dashv b)'(a \dashv b')'$  is found to be never in  $T$ . Postulates 1-17 hold (16 by examination of cases), so that B1-B8 also hold. B9 holds (taking  $a = 3, b = 2$ ). B10 holds. Hence F cannot be deduced from B1-B10.

### §13 COMPARISON WITH "MATERIAL IMPLICATION"

We conclude this paper with a strict formulation of the difference between the system of Postulates 1-17 and the system of "material implication."

The theory of "material implication" in Section A of Whitehead and Russell's *Principia Mathematica* may be regarded as an "abstract deductive theory" dealing with (1) a class of objects  $p, q, r$ , ("elementary propositions"), which we may call the class  $K$ , (2) the assertion sign,  $\vdash$ , (3) a unary operator,  $\sim$  (read "curl"), (4) a binary operator,  $\vee$  (read "wedge"), and three other binary operators, defined in terms of  $\sim$  and  $\vee$ , namely  $\supset$  (read "horseshoe"),  $\times$  (read "times"), and  $\equiv$  (read "triple")

[For typographical convenience we shall replace the prefix " $\vdash$ " by the suffix "in  $T$ ," and also the "curl,"  $\sim$ , by the "dash," ' $,$ ', so that " $\vdash p$ " will appear as " $p$  in  $T$ ," and  $\sim p$  will appear as  $p'$ .]

Postulates \*1 7, \*1 71, \*1 01, \*3 01, \*4 01 of *Principia Mathematica*<sup>10</sup> show that  $p'$ ,  $p \vee q$ ,  $p \supset q$ ,  $pq$ , and  $p \equiv q$  are elements of  $K$ .

<sup>10</sup> The propositions of *Principia Mathematica* cited in this paper are the following

- \*1 1 Anything implied by a true elementary proposition is true
- \*1 7 If  $p$  is an elementary proposition,  $p'$  is an elementary proposition
- \*1 71 If  $p$  and  $q$  are elementary propositions,  $p \vee q$  is an elementary proposition
- \*1 01  $p \supset q = p' \vee q$  Df      \*3 01  $pq = (p' \vee q')'$  Df
- \*4 01  $p \equiv q = (p \supset q) \supset (q \supset p)$  Df

whenever  $p$  and  $q$  are elements of  $K$ , paragraph (3) in \*1 shows that an "asserted" proposition is at any rate a proposition, and \*4.2 (or any other asserted formula) shows that there exists at least one element of  $K$  which is "in  $T$ ". Hence, in our "arrow" notation, we have the following rules of closure on the base ( $K, T, \times, ', =$ )

## RULES OF CLOSURE

- (1)  $p$  in  $K$ . &  $q$  in  $K \rightarrow pq$  in  $K$
- (2)  $p$  in  $K \rightarrow p'$  in  $K$
- (3)  $p$  in  $K$  &  $q$  in  $K \rightarrow p=q$  in  $K$ .
- (4a)  $p$  in  $T \rightarrow p$  in  $K$
- (4b)  $\exists p$  ( $p$  in  $T$ )

That is, our Postulates 1, 2, 3, 4a, 4b hold true in the Principia system if " $=$ " is replaced by " $\equiv$ " [Our optional postulate 4c  $\exists p$  not in  $T$ , is not found in the formal Principia system, except for an "informal" convention, the formal Principia system might consist of only a single element.]

Postulate \*1.1 is a fundamental rule of procedure which may be expressed, in our "arrow" notation, as follows

RULE OF INFERENCE  $p$  in  $T$ . &  $p \triangleright q$  in  $T \rightarrow q$  in  $T$ 

That is, from " $p$  is asserted" and " $p \triangleright q$  is asserted" we may infer " $q$  is asserted". This rule of procedure we shall refer to as "Inf".

The Principia's propositions \*3.2, \*3.33, and \*3.26 (in view of Inf.) yield three further rules of procedure (which we shall refer to as "Adj", "Syll", and "Red")

RULE OF ADJUNCTION  $p$  in  $T$  &  $q$  in  $T \rightarrow pq$  in  $T$ RULE OF THE SYLLOGISM.  $p \triangleright q$  in  $T$ . &  $q \triangleright r$  in  $T \rightarrow p \triangleright r$  in  $T$ RULE OF REDUCTION.  $pq$  in  $T \rightarrow p$  in  $T$ 

- \*2.02  $q \triangleright p \triangleright q$  in  $T$    \*2.11  $p \vee p'$  in  $T$    \*2.21  $p' \triangleright p \triangleright q$  in  $T$ .  
 \*2.521  $(p \triangleright q)' \triangleright q \triangleright p$  in  $T$    \*3.2  $p \triangleright (q \triangleright pq)$  in  $T$   
 \*3.24  $(pp')'$  in  $T$   
 \*3.26  $pq \triangleright p$  in  $T$    \*3.33  $(p \triangleright q) (q \triangleright r) \triangleright p \triangleright r$  in  $T$   
 \*3.35  $p(p \triangleright q) \triangleright q$  in  $T$   
 \*4.11  $p=\!q =\! p'=\!q'$  in  $T$    \*4.13  $p=\!p''$  in  $T$    \*4.2.  $p=\!p$  in  $T$   
 \*4.21  $p=\!q =\! q=\!p$  in  $T$    \*4.22  $(p=\!q) (q=\!r) \triangleright p=\!r$  in  $T$   
 \*4.24  $p =\! pp$  in  $T$   
 \*4.3  $pq =\! qp$  in  $T$    \*4.32  $(pq)r =\! p(qr)$  in  $T$   
 \*4.36  $p=\!q \triangleright (pr =\! qr)$  in  $T$   
 \*4.42  $p =\! (pq \vee pq')$  in  $T$    \*4.53  $(pq)' =\! p' \vee q$  in  $T$   
 \*4.57  $(p'q')' =\! p \vee q$  in  $T$   
 \*4.71  $p \triangleright q =\! (p =\! pq)$  in  $T$    \*4.86.  $p=\!q \triangleright (p=\!r =\! q=\!r)$  in  $T$   
 \*5.21  $p'q' \triangleright p=\!q$  in  $T$ .

Hence our Postulates 5, 6 also hold true in the Principia system.

In the following list, formulas numbered in italics are not explicitly mentioned in the Principia, but are readily deduced by Principia methods from the Principia's postulates, and hence may properly be added to the Principia list

- \*4.03  $(p \equiv q \supset p \supset q)$  in  $T$  (By \*4.01, \*3.26.)
- \*4.46  $[p(p \equiv q) \supset q]$  in  $T$  (By \*4.01, \*4.32, \*3.26, \*4.03, \*3.35, Syll.)
- \*4.36  $(p \equiv q \supset pr \equiv qr)$  in  $T$
- \*4.16  $(p \equiv q \supset p' \equiv q')$  in  $T$  (By \*4.11, \*4.03)
- \*4.86.  $(p \equiv q \supset p \equiv r \equiv q \equiv r)$  in  $T$ .
- \*4.21  $(p \equiv q \equiv q \equiv p)$  in  $T$
- \*4.3  $(pq \equiv qp)$  in  $T$ .
- \*4.32  $[(pq)r \equiv p(qr)]$  in  $T$
- \*4.92  $(p \equiv q \supset rp \equiv rq)$  in  $T$  (By \*4.3, \*4.46, \*4.86, \*4.21, \*4.03, \*4.36, Syll, cf our proof of 24)
- \*4.93  $(p \equiv q \supset r \equiv p \equiv r \equiv q)$  in  $T$  (By \*4.21, \*4.86, \*4.03, Syll, cf our proof of 25)

Hence our Postulates 7–13, with “ $\equiv$ ” replaced by “ $=$ ”, and also our theorems 24, 25, hold true in Principia. Also,

- \*4.2  $(p = p)$  in  $T$
- \*4.26  $(p = q \supset q = p)$  in  $T$  (By \*4.21, \*4.03)
- \*4.22  $(p = q q = r \supset p = r)$  in  $T$

From \*4.36, \*4.92, \*4.86, \*4.93, and \*4.16 we derive (as in our proof of 29) the following further rule of procedure

**RULE OF REPLACEMENT FOR  $=$**  Let  $\xi$  be any expression built up out of parentheses, the letters  $p, q, r, \dots$ , and the signs  $\times, ', \equiv$  in accordance with the closure postulates, so that  $\xi$  stands for an element of  $K$ , and suppose that at some point in the expression  $\xi$  there occurs the letter  $p$ . Then if  $\eta$  is another expression which differs from  $\xi$  only in having this particular  $p$  replaced by  $q$ , we have the rule.

$$(p = q) \text{ in } T \rightarrow (\xi = \eta) \text{ in } T$$

This rule (to be referred to as “Repl”), together with \*4.2, \*4.26, \*4.22, shows that our theorems 26–29 (with “ $\equiv$ ” replaced by “ $=$ ”) hold true in the Principia system. Hence, if we define “ $p = q$ ” as an abbreviation for “ $(p \equiv q)$  in  $T$ ,” the sign “ $=$ ” may be handled, within this system, exactly like the ordinary equality sign in mathematics.

In view of this fact, the following formulas serve as definitions of  $\vee$  and  $\supset$  in terms of  $\times, ', \equiv$ , and  $=$

- \*4 571  $[p \vee q = (p'q')']$  in  $T$  (By \*4 57, \*4 21)  
 \*4 58  $[p \supset q = (pq')']$  in  $T$  (By \*1 01, \*4 53)

Hence, the Principia system may be regarded as built on the base  $(K, T, \times, ', =)$

We also have

- \*4 59  $[(p'q')(p'q')' = p]$  in  $T$  (By \*4 42, \*4 26, \*4 571,  
 \*4 22, \*4 11)  
 \*4 13  $(p = p'')$  in  $T$   
 \*5 26  $(pp' = qq')$  in  $T$  (By \*3 24, \*5 21)  
 \*4 24  $(p = pp)$  in  $T$

Hence our Postulate 14, and the theorems 31, 33, and 36, with " $\equiv$ " replaced by " $=$ ", hold true in Principia. In view of \*5 26 and Repl, we are justified in introducing the letter  $Z$  through the following definition

DEFINITION  $(Z = qq')$  in  $T$

The chief properties of  $Z$  (or  $qq'$ ) are the following

- \*5 27  $[p(qq')' = p]$  in  $T$  (By \*4 59, \*5 26, \*4 3, \*4 24,  
 \*4 13)  
 \*5 28  $[p(qq') = (qq')]$  in  $T$  (By \*4 24, \*4 26, \*4 36, \*4 32,  
 \*4 22, \*5 26)

Hence our theorems 35 and 37 (with  $\equiv$  replaced by  $=$ ) hold true in Principia.

Furthermore, we are entirely at liberty to add the following definitions of  $p^*$  and  $p \dashv q$  to the Principia system, although we shall see in a moment that these definitions are superfluous

- DEFINITION  $[p^* = p \equiv (qq')]$  in  $T$ , or, briefly,  $p^* = (p \equiv Z)$   
 DEFINITION  $[p \dashv q \equiv (pq')^*]$  in  $T$ , or, briefly,  $p \dashv q = (pq' \equiv Z)$

If these definitions are adopted, we find

- \*5 76  $[(p \dashv q)(q \dashv p) = (p \equiv q)]$  in  $T$  (By \*5 38, below, and  
 \*4 01)  
 \*5 77.  $[(p \dashv q)(q \dashv r) \dashv (p \dashv r)]$  in  $T$  (By \*5 38, below, and  
 \*3 33)  
 \*5 78  $[p(p \dashv q) \dashv q]$  in  $T$  (By \*5 38, below, and \*3 35)

Hence our Postulates 15, 16, 17 (with  $\equiv$  replaced by  $=$ ) may be said to hold true in the Principia system

The foregoing considerations may be summed up as follows

13.1 *Regarding the Principia system as an abstract system on the base  $(K, T, \times, ', \equiv)$ , and our system as an abstract system on the base  $(K, T, \times, ', \equiv)$ , we see that all our postulates 1-17 (except 4c), including all our definitions A-D, become valid theorems in the Principia system when  $\equiv$  is replaced by  $=$ . That is, our entire system (with  $\equiv$  replaced by  $=$ ) is a formal part of the Principia system, strictly deducible from the Principia's postulates.*

The converse, however, is not true. There is one postulate of the Principia system which does not correspond to anything in our system, namely, \*4.01, which may be written as follows

$$\ast 4.04 [(p \supset q)(q \supset p) = (p = q)] \text{ in } T \quad (\text{By } \ast 4.01, \ast 4.2)$$

The following important theorems are consequences of \*4.04

$$\ast 5.37 [p = p = (qq')] \text{ in } T \quad (\text{By } \ast 4.01, \ast 4.58, \ast 4.13, \ast 5.28, \ast 5.27)$$

$$\ast 5.38 [p' = p = (qq')] \text{ in } T \quad (\text{By } \ast 4.01, \ast 4.58, \ast 5.27, \ast 5.28)$$

Or briefly (using the notation  $p = q$  for  $p = q$  in  $T$ , and  $Z$  for  $qq'$ )

$$p = (p = Z') \quad \text{and} \quad p' = (p = Z)$$

We now see why the definitions of  $p^*$  and  $p \dashv q$  are superfluous in the Principia system, for, in view of \*5.38 and \*4.58, these definitions become

$$p^* = p' \quad \text{and} \quad p \dashv q = p \supset q$$

We also observe that it is theorem \*5.38 [ $p' = (p = Z)$ ] which is responsible for the so-called paradoxes of the Principia system, such as the following

$$P1 \quad q \text{ in } T \rightarrow (p \supset q) \text{ in } T \quad (\text{By } \ast 2.02)$$

$$P2 \quad p' \text{ in } T \rightarrow (p \supset q) \text{ in } T \quad (\text{By } \ast 2.21)$$

$$P3 \quad (p \supset q)' \text{ in } T \rightarrow (q \supset p) \text{ in } T \quad (\text{By } \ast 2.521)$$

Also, using the notation  $p$  in  $T'$  for  $p'$  in  $T$  (cf. our 53), and the notation  $p = Z$  for  $p = q$  in  $T$ , we have

$$P4 \quad p \text{ in } T \rightarrow p = Z' \quad (\text{By } \ast 5.37)$$

$$P5 \quad p \text{ in } T' \rightarrow p = Z \quad (\text{By } \ast 5.38)$$

where  $Z = qq'$ . That is, all the elements in  $T$  are interchangeable with the unique element  $Z'$ , and all the elements in  $T'$  are interchangeable with the unique element  $Z$ . It should be noted, however, that there is nothing in the formal Principia system to exclude elements which are neither in  $T$  nor in  $T'$  (see our Example B9, above). [It is only an "informal" reading of the formula \*2.11 ·  $p \vee p'$  in  $T$  which

makes it appear that every element of a Principia system must be either in  $T$  or in  $T'$ ]

The essential contrast between the two systems may therefore be summarized as follows

13.2. *The Principia system ( $K$ ,  $T$ ,  $\times$ ,  $'$ ,  $\equiv$ ) and our system ( $K$ ,  $T$ ,  $\times$ ,  $', \equiv$ ) are mathematically identical (that is, isomorphic), when  $\equiv$  is replaced by  $\equiv$ , except that the Principia system includes one additional postulate, which may be stated briefly in the form  $p' \equiv (p \equiv Z)$ .*

In short, the Principia system identifies the two elements  $p'$  and  $p \equiv Z$ , while our system (following Lewis) permits the two elements  $p'$  and  $p \equiv Z$  to be treated as separate entities

Hence, the concept of "material" implication, defined by  $p \supset q = pq' \equiv Z$ , or  $p \supset q = pq \equiv p$  (\*4.71), is less flexible (and for many purposes less useful) than the concept of "strict" implication, defined by  $p \dashv q = pq' \equiv Z$ , or  $p \dashv q = pq \equiv p$  (our 74)

HARVARD UNIVERSITY,

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**POLYMORPHIC TRANSITIONS OF 35 SUBSTANCES TO  
50,000 Kg/Cm<sup>2</sup>**

**By P. W. BRIDGMAN**

**INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WITH AID FROM THE  
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### INTRODUCTION

In a previous paper I have briefly described a new form of high pressure apparatus with which pressures up to 50000 kg/cm<sup>2</sup> may be reached,<sup>1</sup> and I also described the polymorphic transitions of the elements which had been studied with this apparatus. In this present paper the thermodynamic parameters of the transitions of a number of inorganic compounds are given, and also a detailed discussion of a number of matters of technique connected with the new apparatus for which there was no room in the preceding paper.

### DETAILS OF TECHNIQUE

The general scheme of the apparatus is suggested by Figure 1, reproduced from the previous paper. The "cylinder" A in which

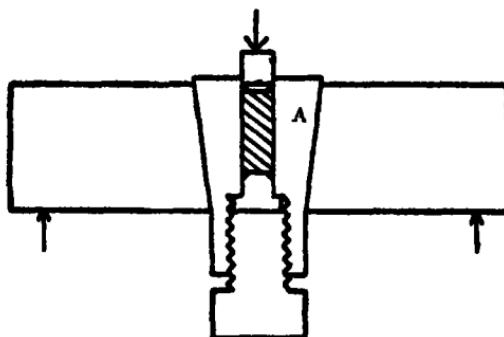


FIGURE 1 Schematic representation of method of automatically subjecting the pressure vessel to external pressure

pressure is produced has a conical external surface, like a stopper. Pressure is produced in this "stopper" by means of the piston P. The thrust exerted on the stopper by the piston is taken up by the conical collar into which the stopper fits, and which exerts an external pressure on the stopper proportional to the total thrust, neglecting friction.

The magnitude of the external pressure on the stopper can be readily calculated. If  $T$  is the total thrust exerted by the piston and

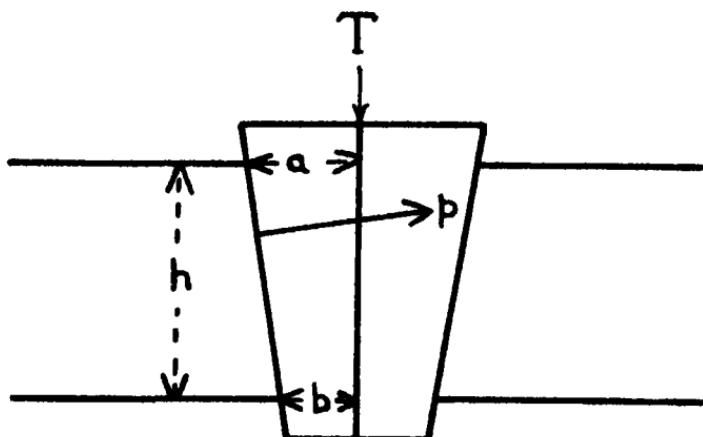


FIGURE 2 Diagram for calculating relation between thrust and external pressure

$p$  the pressure per unit area exerted by the collar, then to a sufficient approximation, for small angles of the cone (see Figure 2)

$$T = p \frac{a - b}{h} h 2\pi \frac{a + b}{2},$$

or

$$p = \frac{T}{\pi(a^2 - b^2)}$$

That is, the pressure exerted by the collar is equal to that which would be produced by the total thrust on the piston concentrated on the annulus corresponding to the difference between the two ends of the cone. In the actual apparatus,  $h = 1$  inch,  $a = 0.516$  inches, and the taper was 1.25 inches per foot (double angle). This makes the area of the annulus 0.100 square inches. The usual diameter of the piston was 0.265 inches, area 0.0552 square inches, so that a pressure on the piston of 50,000 kg/cm<sup>2</sup> produces an external pressure on the stopper of  $\frac{0.0552}{0.160} \times 50,000$  or 17,200 kg/cm<sup>2</sup>

The collar supporting the stopper was made of the same material as most of my previous high pressure cylinders, chrome vanadium

steel, and heat treated in the regular way. The collar was seasoned by a preliminary stretching, by forcing into it a cone, until a permanent set of perhaps 5 per cent was produced. It was then ground to final dimensions. The pressure of approximately 17000 in the collar was as high as I felt could be comfortably used in this grade of steel. It would be possible to somewhat improve on these figures by the use of "Solar" steel, using a somewhat smaller angle for the stopper, and I shall do this when I have a chance to reconstruct the apparatus.

The friction between stopper and collar is a very important matter, and unless precautions are taken, may be so great as to seriously diminish the effectiveness of the external support. The friction may be conveniently evaluated by measuring the distance the stopper is pushed into the collar as a function of the total thrust, with increasing and decreasing thrust. A cyclic curve of the general shape of Figure 3

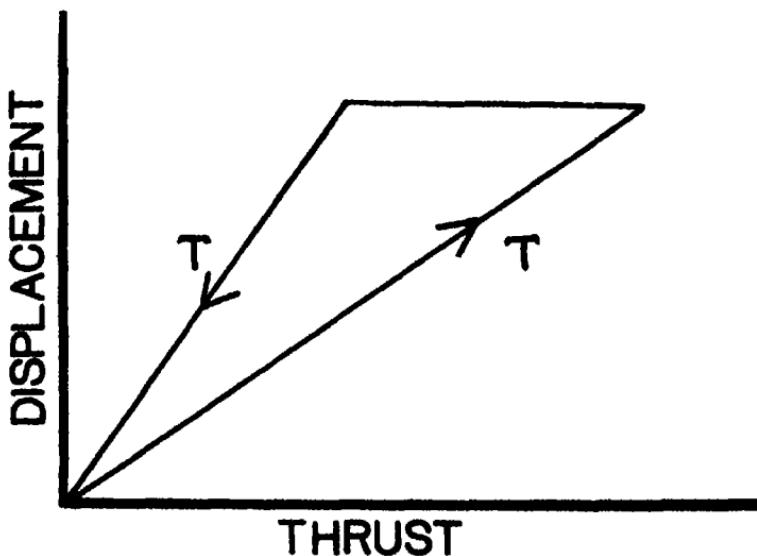


FIGURE 3 The cyclic relation between thrust and displacement of the stopper into its sleeve

will be obtained. The difference between ascending and descending branches is due to friction. The actual thrust corrected for friction may be obtained from the average of the two branches.

The actual coefficient of friction may be easily calculated. Denote by  $N$  the total normal pressure on the external surface of the stopper

$N$  is approximately equal to  $p\hbar\pi(a+b)$  in the former notation. Then during increasing thrust we have

$$T = N \sin \alpha + \mu N \cos \alpha$$

and during decreasing thrust

$$T' = N \sin \alpha - \mu N \cos \alpha$$

We take  $N$  to be a function of the displacement only, so that for corresponding points on the increasing and decreasing branches  $N$  may be eliminated, giving

$$\mu = \frac{T - T'}{T + T'} \frac{\sin \alpha}{\cos \alpha}$$

Suppose, for example, that  $T = 2T'$ , a figure corresponding to conditions easily attained. This gives, since  $\sin \alpha = 0.052$ ,  $\mu = 0.017$ . This is a coefficient of friction lower than values usually given in engineering hand books for conveniently available materials, yet even with this very low coefficient, the effective thrust on the stopper is 0.75  $T$  instead of  $T$ , and the effective external pressure at the maximum, 12,900 kg/cm<sup>2</sup> instead of 17,200. The extreme importance of cutting down the friction to the lowest possible value is therefore evident.

A number of experiments were made in the search for the best method of lubricating stopper and collar. In this search my shearing experiments were of great assistance,<sup>2</sup> as well as my former measurements of the effect of pressure on the viscosity of liquids.<sup>3</sup> Ordinary lubricants cease to function in the familiar ways under conditions of very high pressure. Oils and greases freeze solid, and at high pressures behave effectively like materials with high friction. The shearing experiments had shown that at high pressures the surface friction of practically every solid substance becomes so high that plastic yield takes place in the interior rather than on the surface. The obvious thing, therefore, was to find materials with minimum shearing strength. Materials with low shearing strength are tin, indium, and lead. Indium would be the best, but it is not available for obvious reasons. Lead is a little better than tin. The measurements of the shearing strength of lead indicated a strength almost proportional to the pressure in the significant range, such that the equivalent coefficient of friction is 0.016. This is a trifle lower than in the numerical example just considered. The first improvement consisted in using sheet lead as a lubricant between stopper and

collar. Assembly was made by wrapping a sheet of commercial lead foil 0.002 inches thick around the stopper before inserting the stopper in the collar. In the early work a lubricant of vaseline and graphite was used. This was fairly good, at relatively high pressures graphite loses its lubricating properties, particularly when used alone, but 17000 did not prove high enough to introduce this disturbing effect. However, the sheet lead was a distinct improvement on vaseline and graphite. Further very marked improvement was made by using an additional lubricant between both steel surfaces and sheet lead. Here the experiments on pressure coefficient of viscosity proved valuable. Water and glycerine had both been previously found to suffer comparatively small changes of viscosity with pressure, in fact the initial effect of pressure is to decrease the viscosity of water. After various trials a paste of two thirds glycerine, one third water and enough flake graphite to make it fairly stiff was found to be most effective. Under some conditions this has given coefficients of friction as small as 0.004, using the formula above for  $\mu$ , which means that the external pressure on the stopper is only about 4 per cent less than the theoretical maximum. This is so near the ideal limit that it did not seem worth while to search further.

It is unfortunate that metallic sodium did not prove possible. This metal is so soft that it is very much superior to lead, but I have found that rupture has always followed contact of sodium with steel at high pressures. It is not by any means certain that some of these ruptures were not mere coincidence, but there have been so many of them that I could not help ascribing significance to them and I have therefore given up the attempt to use sodium to transmit high pressures. Perhaps it may be available under other conditions when the pressure is not so high. Lead and glycerine and graphite has the advantage over sodium for these particular experiments that it can be used over a considerably wider temperature range.

The stopper was made of "Solar" steel. This is a silicon manganese steel made by the Carpenter Steel Co., a typical analysis is C 0.50, Mn 0.40, Si 1.00, Mo 0.50. Heat treatment is by quenching into water from 1550° F and then drawing back to 600°, to a Rockwell C hardness of 52 to 54. The manufacturers state that with this heat treatment the tensile strength is over 300,000 lb/in<sup>2</sup>, and the elongation in 2 inches 8%. The steel therefore has a very high tensile strength combined with unusually high elongation. The elongation is so high that the inside of the stopper should stretch before breaking. The fact that this steel is water-hardening imposes the necessity for great care

in heat treatment. The change of dimensions during hardening is unusually high, and I have found a rather greater tendency for cracks to develop during hardening than in the other steels which I have used for high pressures. One useful property of the steel is that even when as hard as 52 it does not glaze the edge of the reamer, so that it is possible to stretch the stopper by a preliminary application of pressure, and then ream to final size, something that is impossible in chrome vanadium steel of as great hardness as this.

The elastic deformation of the stopper may be calculated to a rough degree of approximation by the usual formulas for a cylinder under external and internal pressure. The formula (see for example Love's *Elasticity*, fourth edition, p. 144) for the radial displacement in an infinitely long cylinder is

$$u = Ar + B/r,$$

where

$$A = \frac{p_1 r_1^2 - p_0 r_0^2}{2(\lambda + \mu)(r_0^2 - r_1^2)}$$

$$B = \frac{(p_1 - p_0) r_0^2 r_1^2}{2\mu(r_0^2 - r_1^2)}$$

$p_1$  and  $r_1$  are internal pressure and radius, and  $p_0$  and  $r_0$  the corresponding external quantities. This formula neglects the longitudinal change of dimensions, which may be legitimately done for our purposes. In our case  $r_0 \cong 4r_1$ . Let us put  $p_0 = 0.344 p_1$ , and compare the stretch at the inside surface under these conditions with that in a cylinder with infinitely thick walls subjected to the internal pressure  $p_1$ .

#### Case I (external and internal pressure)

$$A = \frac{p_1}{2(\lambda + \mu)} \left[ \frac{1 - 5.51}{15} \right]$$

$$B = \frac{0.328 p_1}{\mu} \left[ \frac{r_1^2}{1 - 1/16} \right]$$

$$\frac{1}{p_1} \frac{u}{r} \Big|_{r=r_1} = \frac{-4.51}{30(\lambda + \mu)} + \frac{350}{\mu}$$

#### Case II (infinite cylinder under internal pressure only)

$$A = 0, B = \frac{p_1 r_1^2}{2\mu}$$

$$\left. \frac{1}{p_1 r} u \right|_{r=r_1} = \frac{1}{2\mu}$$

Take for numerical values  $\mu = 7.7 \times 10^{11}$ ,  $\lambda = 9.4 \times 10^{11}$  (Abs C G S)

Then, Case I  $\left. \frac{1}{p_1 r} u \right|_{r=r_1} = 0.0366 \times 10^{-11}$

Case II  $\left. \frac{1}{p_1 r} u \right|_{r=r_1} = 0.063 \times 10^{-11}$

In the absence of any other criterion we may take the stretch at the inner surface as a measure of the pressure which the cylinder will stand. By applying external pressure to the finite cylinder we therefore obtain an additional factor of  $63/36.6 = 1.7$  beyond that possible in an infinitely thick cylinder. This factor is in addition to that obtainable by the initial stretching, which gives a factor of the order of 2. In the previous paper it was stated that the previous limit of my high pressure experiments, before using this device of automatic application of external pressure, was  $20,000 \text{ kg/cm}^2$ . The factor 1.7 is obviously not enough to increase the range from 20,000 to 50,000. The new increase of range depends on other factors also. It must be remembered in the first place that 20,000 did not represent the absolute upper limit by any means. By proper preliminary stretching I had already reached pressures above 40,000 in solar steel cylinders 2 inches in diameter. The benefit of this stretching gradually wore away, however. Furthermore, the former apparatus for 20,000 was 4.5 inches in diameter,<sup>4</sup> so that a good deal of time was involved in getting a single cylinder ready for use. These cylinders always ruptured after a number of excursions to 20,000, with possible loss of the enclosed elaborate measuring apparatus. The new apparatus, however, is very much smaller, the stoppers being only one inch in diameter can be made in a short time. The preliminary stretching can be done rapidly, and they can be got into final use a short time after the preliminary stretching. When rupture occurs there is no enclosed elaborate instrument to lose. All these factors are therefore favorable, and the new apparatus can be pushed much closer to the limit than before. The number of excursions possible to 50,000 varies a good deal, there have been a number of instances of 20 or 25 excursions. The limit may be set either by too great stretch of the interior or by fracture. Since the stoppers are so easy to make I have in my later work adopted the arbitrary rule of discarding the stopper after 12 excursions to 50,000.

As already intimated it should be possible to considerably improve on the factor 1.7 by the use of a collar of Solar steel instead of chrome vanadium, permitting the use of smaller angles of the cone and therefore a greater ratio of external to internal pressure. In fact I am now doing this with a very much larger and more elaborate apparatus with which I have reached 30,000 in a true liquid, pressure being

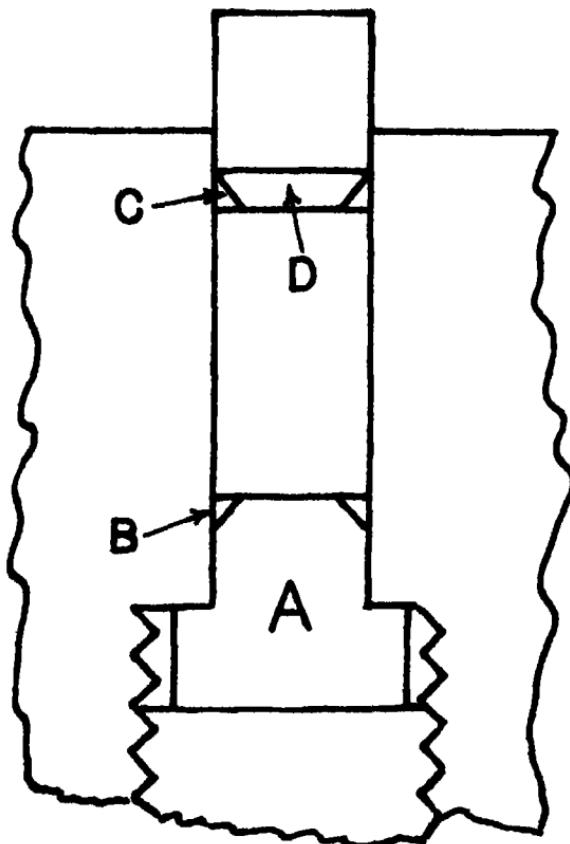


FIGURE 4 Detail of packing

measured with a manganin gauge through insulated leads as in my work at lower pressures

The screw plug with which the stopper is closed at the lower end is a source of weakness. The dimensions are such as to give an adequate

factor of safety according to ordinary methods of computation, but these high stresses cannot be handled according to ordinary rules. It appears as if the thrust cannot be distributed uniformly to all the threads along the length of the screw without a disproportionately greater displacement at the upper end. This has the effect of exceeding the elastic limit in shear of the few threads at the upper end. When pressure has been applied and released a number of times the deterioration of the thread, due to exceeding its elastic limit, gets propagated along the screw until eventually so many threads are affected that all the threads fail by shearing, and the plug is expelled with great violence. A number of very puzzling ruptures of this sort were encountered until the rule was adopted of using each screw plug for only a dozen excursions to the maximum, and since then there have been no failures of this sort. A converse sort of failure may take place if the stopper has been used a great many times with new screw plugs, the upper threads in the stopper give way, probably with the starting of fissures at the bottom of the threads, these fissures propagate themselves, and the whole bottom of the stopper gets torn off. The remedy for both sorts of rupture is to use neither stopper nor plug for more than 12 excursions to the maximum.

The screw plug is made of Cr-Va steel, heat treated by quenching into oil from 1700° F and drawing to 800° F. The central hole in the stopper is closed as shown in Figure 4 on an enlarged scale. The plug *A* is made of a chrome steel suitable for ball bearings (sold under the name of "Teton" by the Ludlum Steel Co.) and is left glass hard, about 65 on the Rockwell C scale. The retaining ring, *B*, is made of Cr-Va steel, heat treated to give a Rockwell C hardness of about 35. The closure at the upper end, which must be capable of moving as the piston advances, is made of a conical ring, *C*, similar to *B*, pushed by a bevelled disc of Teton steel, *D*. The angle on ring and bevel are made slightly different, so that the ring initially bears on the bevel only at its outer periphery.

The piston is a very important part of the apparatus, no steel that I have found will stand a compressive stress of 50,000 kg/cm<sup>2</sup> without continuous slow flow even if it does not immediately fracture. Carboloy proved the solution. I am greatly indebted to Dr Zay Jeffries of the Carboloy Co of America for supplying me with this material. There are a number of different grades of carboloy. Of all those which I tried, that marketed by the Carboloy Co under the designation of No. 905 proved the strongest. The pistons are between 0.250 and 0.315 inches long, and have mostly been used in two diameters, 0.250 and 0.265 inches. The initial internal diameter of the stopper before

stretching is 0.250 inches. The initial stretching is usually combined with measurements on some substance, since the stretch is small and does not vitiate explorations for polymorphic transitions, for this the 0.250 piston is used. The stopper is then reamed to 0.265, and measurements made with the 0.265 piston up to the arbitrarily imposed life of the stopper. In the early work the life of the piston was seldom more than six excursions to 50,000, failure took place by chipping around the upper edge. The support afforded by the interior of the stopper at the lower edge was apparently sufficient to prevent fracture at this place. The piston was pushed at the upper end by a glass hard block of Teton steel ground flat. Taking advantage of the suggestion offered by the fact that the lower edge of the piston does not fracture, in my recent work the upper edge has been reinforced by a ring of heat treated chrome vanadium steel, 0.0625 inches thick, made a force fit for the piston. This is effective in preventing chipping at the upper edge, and the life of the piston is now much longer.

The steel plate which pushes the carboloy piston is of course not as hard as the carboloy, and the elastic limit of the steel is locally exceeded where it is in contact with the carboloy. However the steel is effectively supported by the surrounding parts, and furthermore after several applications of pressure receives an appreciable amount of work hardening (it was a surprise to me that glass hard steel can be work hardened), so that after one or two grindings of the steel surface it need receive no further attention, but apparently is good for unlimited service. Toward the end of the measurements recorded in the following the steel plate has been replaced by an insert of carboloy, 0.50 inches in diameter, ground flat. This is an improvement on the steel, it takes no permanent impression and the upper edge of the piston does not chip.

The stopper was filled with the substance on which measurements were to be made, either completely, or else almost always with the substance placed in some sort of a container. It is an obvious restriction that the substance in contact with the closure ring must be solid. The disadvantage of a solid of course is that it does not transmit a truly hydrostatic pressure. Friction of the solid on the walls of the stopper makes the pressure in the lower part of the stopper less than in the part directly below the moving piston. The error introduced by friction in this way can be roughly computed. Assuming as a crude approximation that the pressure is constant across a section, we have for the equation of equilibrium during increasing pressure

$$\pi r^2 P = (P + dP) \pi r^2 + \mu P 2 \pi r dx,$$

where  $\mu$  is the coefficient of friction and  $x$  is distance along the axis. This gives

$$\frac{dP}{P} = - \frac{2\mu}{r} dx$$

and, on integration  $\log P = - \frac{2\mu}{r} x + C$

Or, putting  $P_0$  for the value of  $P$  at  $x = 0$

$$P = P_0 e^{-2\mu x/r}$$

At the bottom of the cavity  $x/r = 5$ , whence

$$P = P_0 e^{-10\mu}$$

This equation holds in the pressure domain in which surface slip occurs between the walls of the stopper and the material filling it. When pressure rises so high that the shearing strength of the material filling the stopper is reached, the coefficient of friction must be replaced by a corresponding expression involving the shearing strength. Independent measurements of the shearing strength under pressure of many of the compounds investigated here show that the shearing strength is approximately proportional to pressure, so that the substance behaves in the high pressure range as if it had a smaller coefficient of friction than initially, but otherwise in the same way. The shearing measurements have shown that an equivalent coefficient of friction in the domain of plastic flow of 0.1 is not uncommon, so that for such substances the pressure in the bottom end of the stopper would be about one third ( $e^{-1}$ ) of that exerted by the piston on the upper end. It appears then that the effectiveness of the support afforded by friction may in many cases be prohibitively great, and it is obvious that no satisfactory measurements can be made with such substances completely filling the stopper. Lead, however, has a much lower shearing strength, and therefore a much lower equivalent coefficient of friction. The device was therefore adopted of enclosing most of the materials in a sheath of lead. The effective coefficient of friction is now that of the lead, which we have already seen to be 0.016. The factor by which the pressure at the bottom is less than at the top is now  $e^{-0.16} = 0.85$ . The error is larger than desirable, but not intolerable, the mean pressure in the stopper being 7 per cent less than the maximum. In the following experiments this error is very materially further reduced as far as those phenomena are concerned which are of special interest here. During the progress of a transition,

the substance is effectively capable of supporting no stress difference, so that at this particular point the correction for friction does not apply, and the values of equilibrium pressure and of change of volume at this point are not affected.

The method for detecting a transition and for measuring its parameters was the same as in my previous work, namely the displacement of the piston is determined as a function of pressure at constant temperature. The transition is shown by a discontinuity in the curve. The pressure of the discontinuity is now determined at different temperatures, giving the transition curve. From the magnitude of the discontinuity the change of volume may be calculated. From these data the latent heat may also be computed by Clapeyron's equation.

In determining the change of volume corrections have to be applied for the change of cross section of the stopper under pressure. This correction can be computed only roughly because in the first place the boundary conditions are not well defined, and in the second place the mathematical problem in the theory of elasticity is very complicated if one takes exact account of the fact that we are here concerned with a short cylinder in which considerable support is afforded by the ends, which are not subject to internal pressure. The solution for an infinite cylinder already used on page 51 was made the basis of the correction. The distortion produced by the external pressure, which altogether is only a small part of the total effect, was diminished by 10 per cent to allow for friction in the collar. The total distortion then calculated to arise from both external and internal pressure in an indefinitely long cylinder was arbitrarily diminished by 25 per cent, this being my guess as to the magnitude of the effective support by the ends. There results a correction factor of 1.0087 on the cross section per 10,000 kg/cm<sup>2</sup> internal pressure when the diameter of the stopper is 0.250 inches, and 1.0085 when the diameter is 0.265. These two corrections are so close that a single correction, 1.0086 per 10,000 was used for both diameters. This is the correction to be used in computing  $\Delta v$  from the displacement of the piston. The pressure calculated from the total thrust on the piston must also be corrected for expansion of the cross section. This correction was taken as one half that just given, namely 1.0043, the reason for the factor one half being that the cross section at the ends of the region exposed to internal pressure cannot be expanded as much as the average, the shape of the internal cavity under pressure being somewhat like that of a barrel.

The total thrust on the piston was calculated from the areas and the pressure on the piston of the hydraulic press. This press was of exactly the same construction as one described in a preceding paper on shearing, and the pressure on the piston of the press was also measured with an absolute piston gauge, as there described. Friction

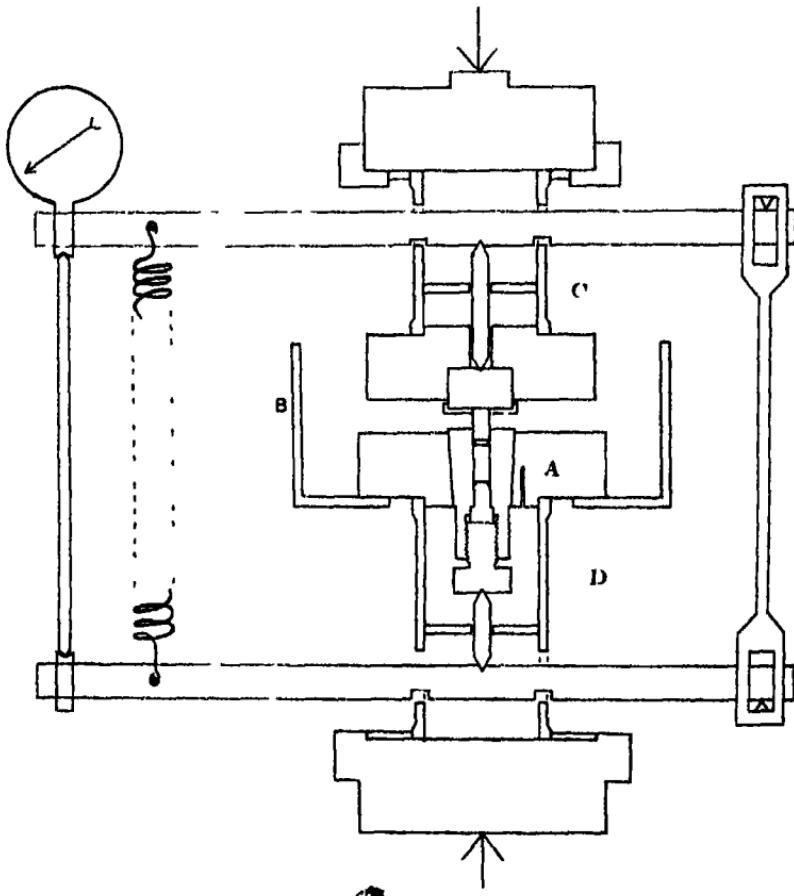


FIGURE 5 General assembly. The arrows top and bottom indicate where pressure is applied by the hydraulic press.

in the press itself was only one or two percent, as established by direct experiment. In addition to friction in the press, no doubt a very appreciable friction was offered by the conical closure immediately under the carbonyl piston. All pressures recorded in the following,

unless otherwise mentioned, are means with increasing and decreasing pressure, so that frictional errors should be approximately eliminated

In measuring the displacement of the piston during a transition a complication is introduced by the fact that the stopper in which the transition is running is itself being displaced into the supporting collar as pressure increases, so that the desired result cannot be obtained merely by measuring the displacement of the hydraulic press, as was possible in my former work. The method by which the displacement of the carboloy piston was obtained is shown in Figure 5, which gives the assembly. This diagram describes sufficiently well the arrangement of the levers by which the displacement of the carboloy piston into the stopper was measured. The levers rest against various supports, not shown, to impart the necessary stability. The motion at the end of the levers was measured with an Ames dial gauge, as shown. The magnification of the lever system was directly determined by replacing the whole central combination, stopper, carboloy piston etc by a micrometer and determining the motion of the Ames gauge for a known motion of the micrometer. The magnification was 2.61. The Ames gauge is directly graduated to 0.001 inch, and the divisions are large enough to permit an easy estimation of tenths. A displacement of the carboloy piston of 0.00004 inches was therefore detectable. Surprisingly consistent readings were obtained, the curves of piston displacement against pressure were often smooth to about the limit of sensitiveness of the readings, the total displacement for 50,000 kg/cm<sup>2</sup> was usually between 0.1 and 0.2 inches.

In addition to the displacement of the carboloy piston, the displacement of the piston of the hydraulic press was always read as a matter of routine. This was determined from a second Ames gauge reading to 0.0001 inch by estimation, attached to the press. These readings occasionally proved useful in distinguishing between a transition and a leak (which seldom occurred), and always by taking the difference of the displacements of the two pistons provided a method of finding the displacement of the stopper into its collar, and from this permitted a determination of the friction between stopper and collar.

Temperature could be varied by means of the oil bath indicated at *B* in Figure 5. This bath was contained in a small sheet iron can, accurately machined and made a forced leak-proof fit for the outer part of the collar. In Figure 5 an earlier arrangement, not so good, is shown, in which the bath is soldered to the collar. Equality of temperature throughout the bath was maintained with four turbine stirrers, of about 0.5 inch diameter, driven at a high speed. Heating

was by resistance coils, spaced uniformly in the annular space outside the collar. There was no thermostatic control, but temperature was maintained constant to better than a degree by manual control, when necessary, of external resistances in the heating circuit. Temperature was determined from a copper-constantan thermo-couple inserted in the small hole *A* drilled in the collar. The temperature was read from the double deflections of a short period galvanometer. The couple was calibrated up to 200° against a mercury thermometer.

Pressure was transmitted to the carboloy piston by means of the steel sleeves *C* and *D*. These were made of heat treated Solar steel, of as small a cross section as was compatible with safely transmitting the compressive force. The purpose of these steel sleeves is to prevent as far as possible heat leak from the temperature bath, and to permit as uniform a temperature as possible in the specimen inside the stopper. The sleeves were accurately made, ground true after heat treatment. It is obvious that a high degree of precision is necessary in the machine work in order to prevent any side thrust on the carboloy piston, which is brittle under any force except a uniform compression.

The temperature was never pushed above 200° at 50,000 kg/cm<sup>2</sup>, at this temperature the steel becomes perceptibly softer and also the carboloy piston is weaker. Some measurements were carried down to -80°, the oil in the bath being replaced for this purpose by a mixture of solid CO<sub>2</sub> and alcohol. Most transitions are too sluggish at this temperature to make measurements practical, however, and the lowest temperature of most of the measurements was room temperature.

Rupture of one sort or another is not an infrequent occurrence. The subsequent splashing of hot oil would have serious consequences, so that the entire apparatus was surrounded with a box of tinned sheet iron, with appropriate slits for the magnifying levers, the belt driving the stirrers, etc.

The routine steps of a transition exploration and measurements were as follows. The apparatus was first filled. Lead sleeves were provided to hold the material, the wall thickness of the sleeve being about 0.8 mm. The material, usually initially in a powdered condition, was placed in the sleeve in the form of little pellets which were previously compressed in a mold of alloy steel in an arbor press to a pressure between 15,000 and 20,000 kg/cm<sup>2</sup>. The principal difficulty with these pellets was in removing them from the mold after formation. If the material has a high coefficient of friction or a high shearing strength it is likely to split up into a great many discs on pushing

out of the mold. For such substances the remedy is to grease the walls of the mold with a small quantity of graphite and vaseline, too small in amount to introduce appreciable error into the measurements. Sometimes even this was not successful, in such cases it was necessary to compress the powder directly into the lead sheath, which was then supported on the outside with another mold. This procedure was adopted only when absolutely necessary, it being difficult because of squeezing out of lead. When the lead sheath had been filled it was coated on the outside with a piece of copper foil 0.001 inch thick. The function of the copper was to keep the lead from direct contact with the steel. A number of unexplained ruptures had raised the suspicion that at these high pressures lead is forced into the steel, attacking it in the same way as mercury is known to do at lower pressures.<sup>6</sup> This precaution has apparently been effective. The lead sleeve with its copper coating was now placed in the stopper and consolidated again in the arbor press to a pressure of perhaps 20,000 kg/cm<sup>2</sup>. Since the carboloy piston is limited in stroke it is necessary to fill the stopper so completely that the piston enters by an amount only just sufficient to keep it centered during assembly. Volume could be built up when necessary by adding bits of lead or thin stamped discs of copper above the sleeve and its contents.

In assembling the apparatus an auxiliary device or two is demanded, but it is not necessary to describe these in detail. The first run was then made at room temperature. A seasoning run was first made. At first this seasoning application of pressure was pushed only to 20,000, but it was found that on the next application of pressure irregularity of some sort always appeared in the neighborhood of 20,000, so that lately I have adopted the practice of seasoning over the entire range of 50,000. The steps in this seasoning application are 4000, and readings are made both with increasing and decreasing pressure. The zero is always displaced by a comparatively large amount after this seasoning application. If the seasoning run displays features of interest, a more careful application of pressure is then made, this time usually in steps of 2000 and at two minute intervals, although sometimes 1000 steps were used. There is always some creep after an increase of pressure, due either to slow yielding against friction or to after effects in the steel, so that it is necessary to adhere to a careful time schedule to obtain smooth readings. A two minute schedule was usually used, pressure was increased every two minutes by adding the proper weight to the dead weight piston gauge and manipulating the hand pump. One minute after increase of pressure both displacement gauges were read, and then again when

two minutes had elapsed. Pressure was then at once increased by another 2000. The dimensions of the apparatus are so small that two minutes is entirely adequate for dissipation of the heat of compression. The pressure increments in the seasoning runs were made at one minute intervals and only the one displacement reading made, at the end of the minute. In plotting the results, both the one and two minute displacements were shown. A transition is shown ideally by a discontinuity in the curve of displacement against pressure, but most transitions are sluggish, particularly at room temperature, and the corners of the discontinuity are often so much rounded, or the discontinuity itself may be so small in amount, that it is difficult to be sure of it. In such instances the creep in the readings between one and two minutes may afford welcome assistance, the creep being larger during a transition. If, after plotting the results there was reason to suspect a transition, measurements were then repeated more carefully in the neighborhood of the transition to determine its parameters more exactly. If the discontinuity was large enough, the most important datum was the equilibrium pressure, approached both from above and below. For example with increasing pressure a displacement was made corresponding to the half complete transition, the piston gauge was clamped, and pressure was allowed to spontaneously fall to its final value, determined by plotting the pressure reading on the Bourdon gauge of the hydraulic press against time. When a steady value was reached, the piston gauge was unclamped, pressure was increased, and enough readings made in the domain of the high pressure phase to enable the discontinuity in the displacement to be determined. Pressure was then decreased and the corresponding readings made. The pressure of the transition was taken as the mean of the pressures reached automatically from above and below. In many cases, however, the volume change was so small, and the amount of excess pressure necessary to start the transition so great that it was not possible to make readings of pressure on the two phase system. In such cases the transition pressure has to be taken as the mean of the pressures at which the transition spontaneously starts with increasing and decreasing pressure respectively. This value is, of course, not as accurate as the other, being obviously in error if the excess pressure required to start the transition is not symmetrical on both sides of the transition.

After the run at room temperature the oil bath was put in operation. If no transition had been found at room temperature the temperature was now set at 150° C., and a similar exploration made up to 50,000 and down. If no transition was found here either, then the substance

was set aside. If a transition had been found at room temperature, then of course measurements were made at a sufficient number of other higher temperatures to establish the phase diagram.

It is difficult to set any general estimate on the magnitude of the transitions which could be detected with this apparatus. Sometimes, when the substance has high friction, the results are much more irregular than in other cases. Some estimate of the sensitiveness can be obtained in the following from the consistency of the values for  $\Delta v$ .

In addition to measurements with the "stopper" apparatus, with which the volume changes are determined, all these substances were also examined with the shearing apparatus described in a previous paper.<sup>6</sup> Many of these shearing results are described in the following since they are pertinent in giving information about some of the properties of the new phases. Precise agreement must not be expected between the transition pressures found in the shearing and the volume apparatus, since shearing stress has a specific effect in displacing the pressure of a transition.

The presentation of detailed data now follows.

#### DETAILED DATA

*Cu<sub>2</sub>I<sub>2</sub>*. This was "c.p." stock from Eimer and Amend. The shearing curve exhibited a very pronounced maximum followed by a deep minimum, leading to the expectation of a transition.

With the volume apparatus a single transition was found with volume change large enough to permit setting on equilibrium with both phases present. This is one of the rather rare substances for which good readings could be made at solid CO<sub>2</sub> temperature. It is also unusual in that the width of the region of indifference becomes larger again at higher temperatures after having passed through a minimum near room temperature. The experimental points are shown in Figures 6 and 7, and the transition parameters in Table I.

TABLE I  
TRANSITION PARAMETERS OF Cu<sub>2</sub>I<sub>2</sub>.

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
16,400	-100	- 0.695	0.0705	20.5	48
15,560	-50	- 0.695	0.0698	26.1	61
14,720	0	- 0.695	0.0675	31.0	74
13,880	50	- 0.695	0.0640	34.2	80
13,040	100	- 0.695	0.0568	35.6	83
12,200	150	- 0.695	0.0480	34.1	80

*AgCl* The material was "c p" stock, obtained from Eimer and Amend. In the shearing apparatus indications of a transition had been found in the neighborhood of 13,000 kg/cm<sup>2</sup>. Measurements were made in the volume apparatus only at room temperature and 150°, and only with increasing pressure. The change of volume is

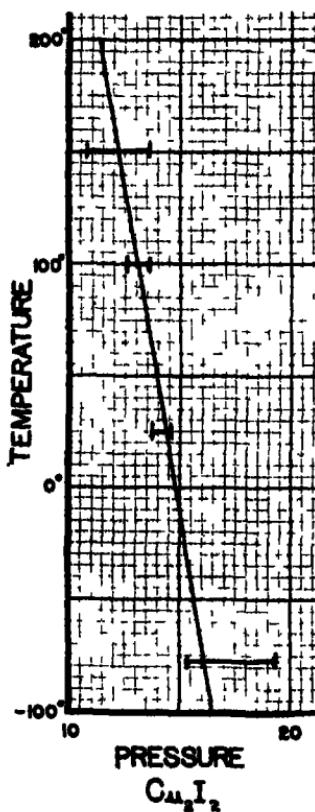


FIGURE 6 The transition line of  $\text{Cu}_2\text{I}_2$ , pressure in thousands of  $\text{kg}/\text{cm}^2$  against Centigrade temperature

small. At room temperature the transition is smeared out through two pressure steps, that is, through 4,000  $\text{kg}/\text{cm}^2$ , but at 150° it ran completely on passing from one step to the next. The volume change at both temperatures was essentially the same, 0.00010  $\text{cm}^3/\text{gm}$ . At 29° a rough value for the transition pressure is 13,000

$\text{kg/cm}^2$ , and at  $150^\circ$  25,000. The latent heat demanded by these data is about 0.08 gm cal/gm.

There was no perceptible change of slope of the displacement curve at the transition, this means that the two modifications have no large difference of compressibility.

*AgBr* The material was "c p" stock from Eimer and Amend. The shearing measurements showed no sharp break in direction, but a region of abnormal upward curvature, beginning at about 25,000

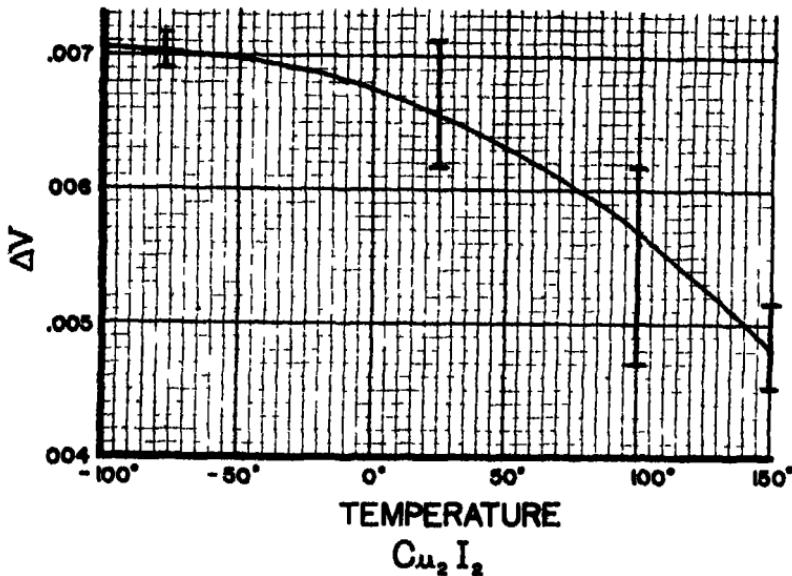


FIGURE 7 The volume change of the transition of  $\text{Cu}_2\text{I}_2$  in  $\text{cm}^3/\text{gm}$  plotted against Centigrade temperature

$\text{kg/cm}^2$ , and suggesting a transition. In the volume apparatus runs were made at room temperature,  $100^\circ$  and  $146^\circ$ . As in the case of  $\text{AgCl}$  the volume change is small, and it is difficult to disentangle the transition from other irregularities. The best values for the transition pressure were 13,000  $\text{kg/cm}^2$  at  $20^\circ$ , 18,800 at  $100^\circ$ , and 28,500 at  $146^\circ$ . The change of volume is independent of temperature within the limits of error and is 0.00015  $\text{cm}^3/\text{gm}$ . The general character of the transition is much the same as for  $\text{AgCl}$ . Since  $\text{AgCl}$  and  $\text{AgBr}$  both have the same type of crystal structure ( $\text{NaCl}$  cubic type) the similarity of the results for both lends probability to the correctness of either

The latent heat demanded by the above data is about 0.14 gm cal/gm at a mean temperature

It is interesting that these two substances of NaCl type structure have transitions with such very small change of volume. The change from NaCl to CsCl type, which is produced by pressure in the ammonium, potassium, and rubidium halides, is accompanied by a large change of volume, so that a similar transition might have been expected here. Perhaps this transition is similar to the curious transition of RbCl with small volume change at low pressures?

$\text{Ag}_2\text{S}$  The material was from Kahlbaum. The shearing curve was of the conventional type, concave toward the pressure axis over the entire range, and with a rather definite knee. There was some slight irregularity beyond the knee that might have been taken to indicate the possibility of a transition, but the effects were very small and the transition most doubtful.

Runs were made in the volume apparatus at four temperatures from room temperature up to  $188^\circ$ . There is a transition with small change of volume, too small to permit settings to be made on the two phase system. At room temperature the transition was not found at all, doubtless because of too great sluggishness. At the higher temperatures the volume change during decrease of pressure was more abrupt than with increasing pressure, giving better values for change of volume with decreasing pressure. The values for change of volume were in any event uncertain enough, and justify only one significant figure, the accuracy does not justify the attempt to deduce what the variation of change of volume is along the transition line.

TABLE II  
TRANSITION PARAMETERS OF  $\text{Ag}_2\text{S}$

Pressure $\text{kg}/\text{cm}^2$	Temperature $^\circ\text{C}$	$\frac{d\tau}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm}/\text{gm}$	Latent Heat $\text{gm cal}/\text{gm}$
15,300	100	0.135			
19,000	150	0.135	0.005	16	0.4
22,700	200	0.135			

The experimental points for transition pressure as a function of temperature are shown in Figure 8. It is not worth while showing a diagram for the change of volume. The transition parameters are given in Table II, assuming a constant and very rough value for volume change.

$\text{Ag}_2\text{S}$  is known to have a polymorphic transition at atmospheric pressure at  $180^\circ$ . This is so near the maximum temperature of these

measurements that one could not expect to find the transition, and it is obvious that the transition studied here is not the same and is new  $ZnBr_2$ . This was "c p" stock from Eimer and Amend. It is very

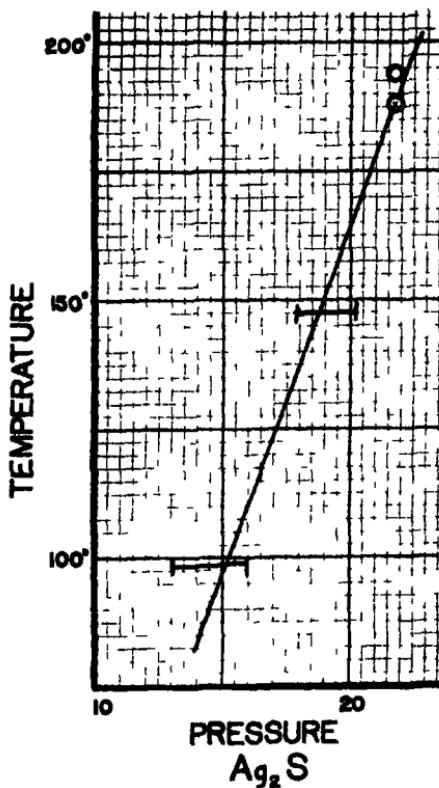


FIGURE 8 The transition line of  $Ag_2S$ , Centigrade temperature against pressure in thousands of  $kg/cm^2$

hygroscopic, it was dried by heating in vacuum to  $130^\circ$  and immediately placed in the pressure vessel

The shearing curve had shown a very marked maximum at about  $26,000\text{ kg}/cm^2$  at room temperature of a character that almost certainly meant a transition or else decomposition to the metal

In the volume apparatus a transition was found at once in the expected place with a comparatively large volume change. Measure-

ments were made at five temperatures from room temperature up to  $150^{\circ}$ . There was some irregularity in the high pressure readings which raised the suspicion that there might be two transitions close

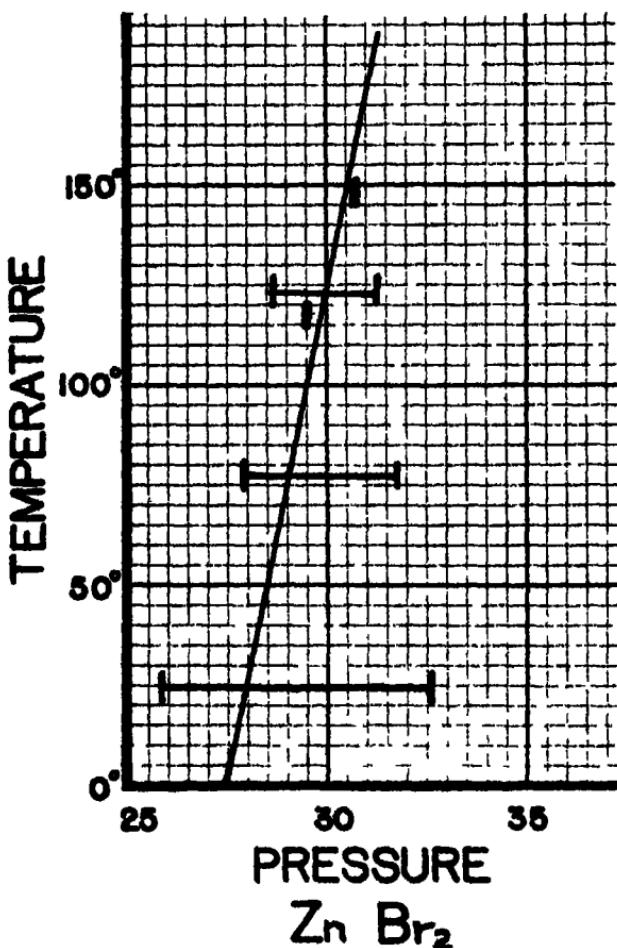


FIGURE 9 The transition line of  $\text{ZnBr}_2$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

together I was not able to obtain any positive evidence that this is the case, but I believe that the possibility is not entirely excluded. At the low pressure end at the higher temperatures there were also

marked irregularities. The interpretation finally adopted for these irregularities is that there is a transition at atmospheric pressure in the neighborhood of  $125^{\circ}$ , which at  $150^{\circ}$  runs at something of the order of  $1500 \text{ kg/cm}^2$  and with a volume change of the order of  $0.01 \text{ cm}^3/\text{gm}$ . This apparatus is not adapted to good measurements in this range, and I let the matter go without trying for improved

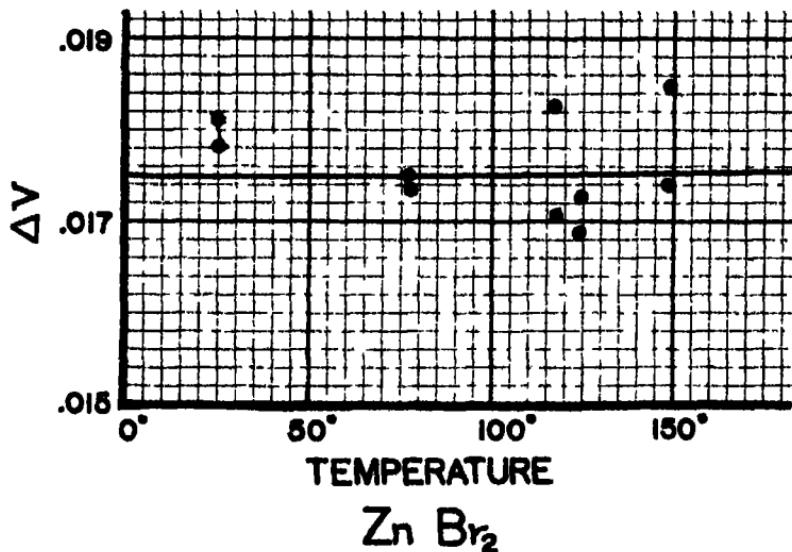


FIGURE 10 The volume change of the transition of  $\text{ZnBr}_2$  in  $\text{cm}^3/\text{gm}$  plotted against Centigrade temperature

values in another apparatus. No previous record seems to have been made of a transition at atmospheric pressure according to Mellor.

The experimental results for the high pressure transition are shown in Figures 9 and 10, and the transition parameters are collected in Table III.

TABLE III  
TRANSITION PARAMETERS OF  $\text{ZnBr}_2$

Pressure $\text{kg/cm}^2$	Temperature $^{\circ}\text{C}$	$\frac{dt}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	Latent Heat $\text{gm cal/gm}$
27,500	0	+ 0500	0175	96	2 24
28,500	50	+ 0500	0175	113	2 66
29,500	100	+ 0500	0175	131	3 06
30,500	150	+ 0500	0175	148	3 47

$HgCl_2$  The material was "c p" stock from Eimer and Amend. The shearing curve did not give any striking evidence for a transition, there was however, a gentle inflection above the knee in the curve at 25,000 which suggested the possibility. Four different fillings of the pressure apparatus were made. With the first filling runs were made at room temperature to 50,000 and back, and at  $150^\circ$  to 45,000, where there was an explosion, the stopper pulling apart at the root of the

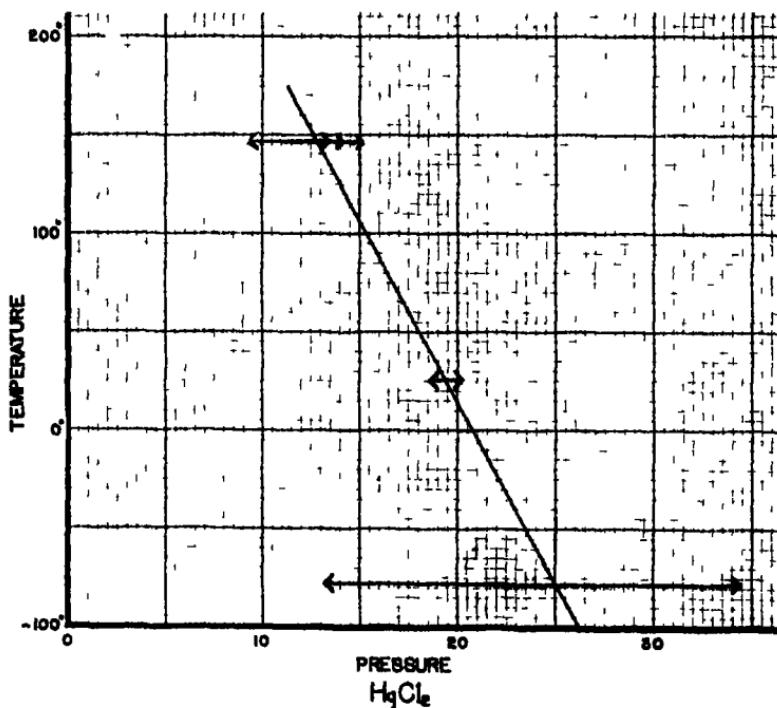


FIGURE 11 The transition line of  $HgCl_2$ , Centigrade temperature against pressure in thousands of  $kg/cm^2$

lower thread. With this run the existence of the transition was established. Values of  $\Delta v$  were found at room temperature, both with increasing and decreasing pressure, although the transition was somewhat sluggish and therefore spread over a range, at  $150^\circ$  a good sharp volume discontinuity was obtained. With the second filling at  $150^\circ$  the stopper ruptured again in the same way at about 30,000, but not until readings had been made on the transition. The third

filling gave readings on the transition at 150°, both with increasing and decreasing pressure, but there was so much creep that I thought it advisable to make a blank run with lead to determine if possible the

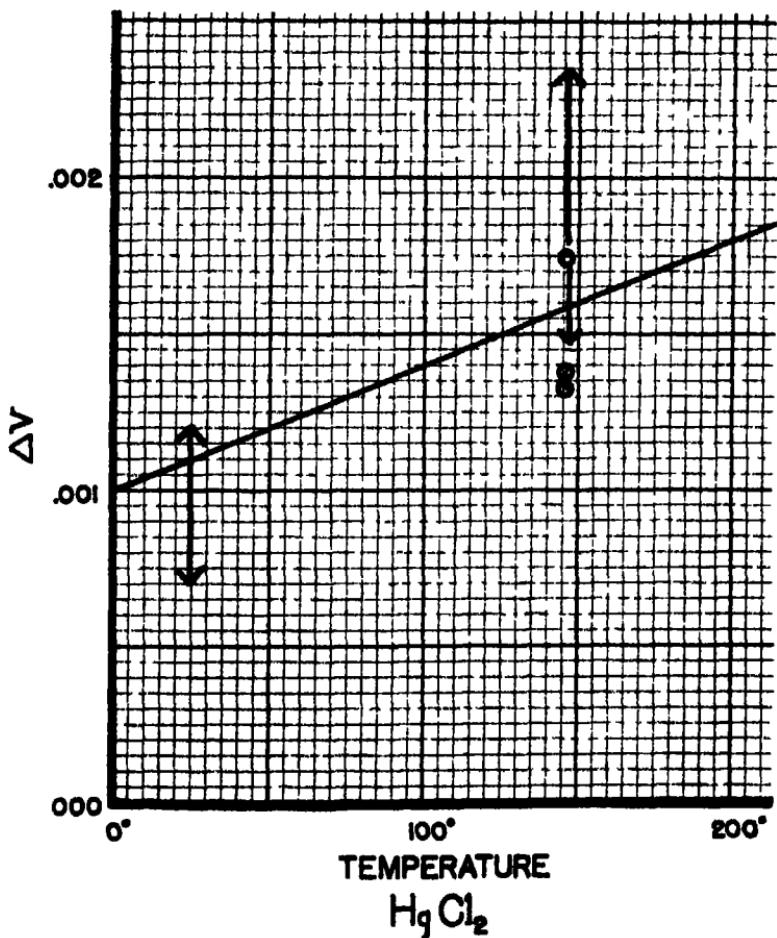


FIGURE 12 The volume change of the transition of  $\text{HgCl}_2$  in  $\text{cm}^3/\text{gm}$  plotted against Centigrade temperature

cause of the creep. This blank run was again terminated by the same sort of rupture. This type of rupture was traced to the screw plug, which had been used so many times that the threads were beginning to shear off. As already explained, the remedy is to use the screw

plug for only a limited number of excursions to the maximum. A fourth set-up and run was now carried out without rupture of the stopper. The last run with this set-up was made at  $\text{CO}_2$  temperature. Here the transition could be detected, principally by increased creep, but the transition was so sluggish, and the corners of the displacement curve so rounded that good values of  $\Delta v$  could not be obtained. The final run was at  $150^\circ$ . This gave good values for the transition pressure and for  $\Delta v$  both with increasing and decreasing pressure. At pressures beyond the transition it was found, however, on plotting the results, that there had been mechanical interference with free motion of the lever giving the piston displacement, so that none of these runs have yet answered the question of whether there may not be still another transition at  $150^\circ$  at pressures above the maximum at which satisfactory readings were obtained, that is, about 45,000.

The experimental results are shown in Figures 11 and 12 and Table IV. The transition is of the ice type. A  $\Delta v$  increasing with increasing pressure is common with this type of transition.

TABLE IV  
TRANSITION PARAMETERS OF  $\text{HgCl}_2$

Pressure $\text{kg/cm}^2$	Temperature $^\circ\text{C}$	$\frac{dv}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	gm cal/gm
20,800	0	- 0183	0010	14 9	35
15,300	100	- 0183	0014	28 6	67
12,600	150	- 0183	0016	37 0	87

$\text{HgBr}_2$ . The source of the material was Eimer and Amend, "c p" stock. The shearing measurements showed two downward breaks, one in the vicinity of 12,000 and the other in the vicinity of 25,000. Beyond the last break the shearing curve was very markedly concave upward, an unusual effect. Both of these breaks are similar to the "knee" shown by normal substances, so that the interpretation of the curves in terms of a transition is difficult.

In the volume apparatus three new modifications were found, with three transition lines running nearly vertically. With the regular volume apparatus exploration was made to 50,000. In all, eight different runs were made with this apparatus, with a single filling, without accident. At the conclusion of the runs a small drop of free mercury was found, indicating some decomposition. The amount of decomposition was so small, however, that there should be no appreciable error in the results. The low pressure transition runs at pressures so low that it could not be measured accurately enough with the

regular apparatus. Accordingly this transition was measured in a similar apparatus with piston 0.375 inches in diameter instead of 0.265. Six different runs were made with this apparatus. No decomposition to free mercury was observable, suggesting that the effect found with the other apparatus was the result of high pressure. This transition becomes rapidly sluggish at low temperatures.

The experimental results are shown in Figures 13 and 14, and the best values of the transition parameters in Table V.

TABLE V  
TRANSITION PARAMETERS OF  $\text{HgBr}_2$

Pressure $\text{kg/cm}^2$	Temperature $^\circ\text{C}$	$\frac{d\epsilon}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	Latent Heat $\text{gm cal/gm}$
I-II					
1,700	50	0.167	0.0185	3.57	084
2,000	100	0.167	0.0185	4.15	097
2,300	150	0.167	0.0185	4.71	110
2,600	200	0.167	0.0185	5.26	113
II-III					
23,000	50	0.455	0.0112	7.9	186
24,100	100	0.455	0.0102	8.4	196
25,200	150	0.455	0.0092	8.5	200
III-IV					
39,200	0	-0.937	0.0204	5.9	139
38,700	50	-0.937	0.0219	7.5	177
38,100	100	-0.937	0.0235	9.3	219
37,600	150	-0.937	0.0250	11.3	264

The phase diagram of  $\text{HgBr}_2$  is seen to be entirely different from that of  $\text{HgCl}_2$ . This is to be expected from the crystal structure. According to Wyckoff, although both belong to the ortho-rhombic system, the space groups are different,  $\text{HgCl}_2$  is a molecular lattice, while  $\text{HgBr}_2$  is a layer lattice.

*HgI<sub>2</sub>*. The material was from the stock room of the Harvard Chemical Laboratory. This substance has a known transition at atmospheric pressure at 127°, where the ordinary red modification changes to yellow. I have previously studied this transition up to 12,000  $\text{kg/cm}^2$ . It is the only transition found so far which has a maximum transition temperature, beyond 5,000  $\text{kg/cm}^2$  and 181° the transition line falling with increasing pressure. The transition becomes very sluggish on the falling branch, however, and I did not follow it beyond 60°. Four runs were made with the present appa-

ratus, at room temperature, 100°, and two at 146°. The known transition from red to yellow was found at all temperatures, with values for the transition pressure and change of volume which agreed with the former values within the limits of error everywhere except for the change of volume at 146°, which was now found somewhat

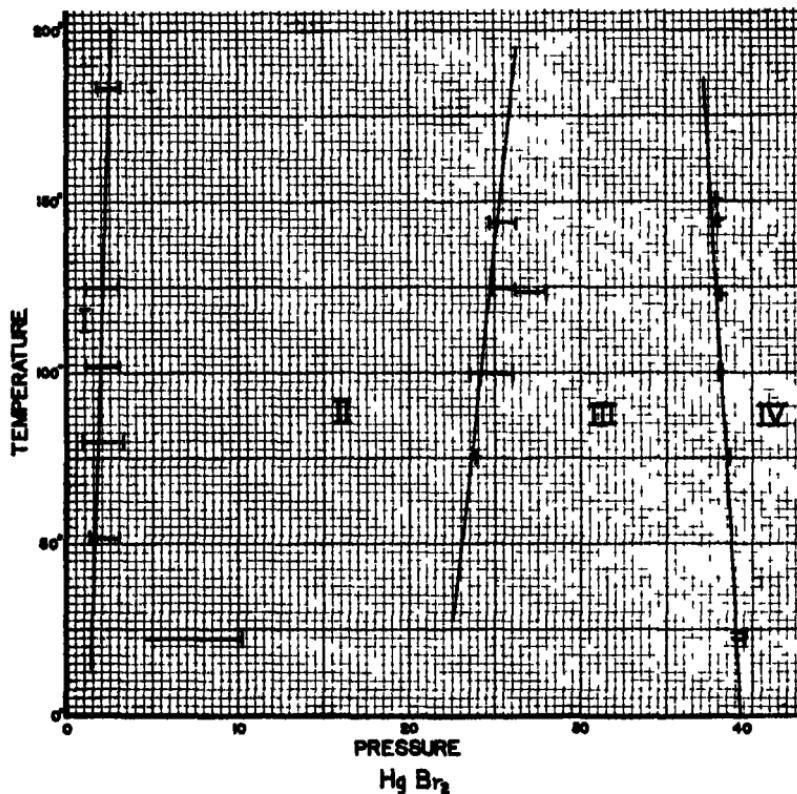


FIGURE 13 The phase diagram of  $\text{HgBr}_2$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

higher than before. At room temperature the difference of transition pressure from above and below was only 1,000 kg, and the transition was not particularly sluggish. The sluggishness of a transition may be affected by many factors, it may be that the lead sheath in which the material was enclosed accounted for the present greater liveliness of the transition.

The greatest interest of these measurements of course lies in the possible discovery of other transitions. Both runs at  $146^{\circ}$  gave evidence for a small transition so near the upper end of the pressure range that with increasing pressure the volume change could not be

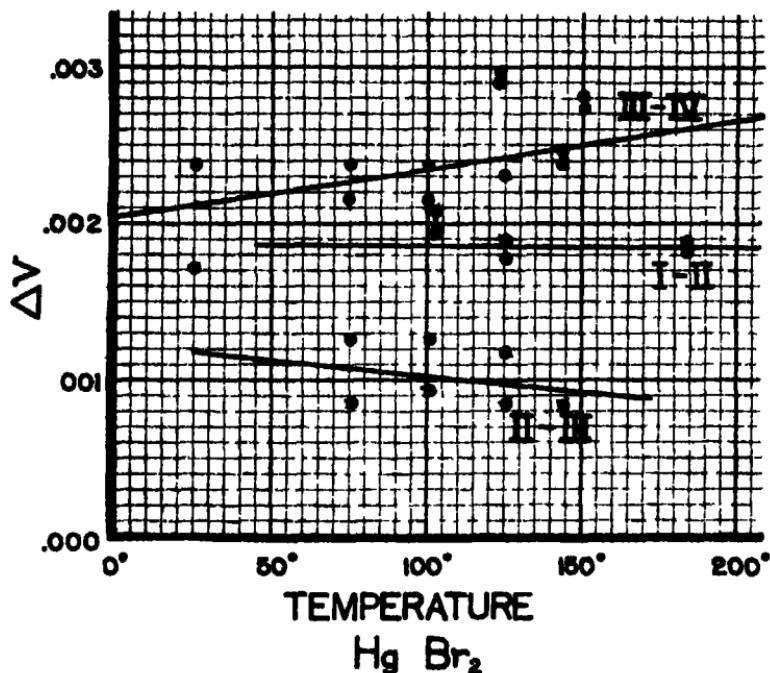


FIGURE 14 The volume change of the transitions of  $\text{HgBr}_2$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature. The apparently scattered points are to be associated with the nearest line

disentangled from creep, which occurred with the particular stopper used for this exploration at a pressure lower than usual. The best values for the pressure of transition at  $146^{\circ}$  are 41,300 to 43,600  $\text{kg}/\text{cm}^2$ , and the volume change is of the order of  $0.0004 \text{ cm}^3/\text{gm}$ . This transition was not picked up at either of the other temperatures, so the latent heat cannot be computed.

The shearing curve had three possible small breaks, the significance of which is most doubtful, but in addition there was one very well defined upward break, of the character that almost invariably means a transition, at  $25,000 \text{ kg}/\text{cm}^2$ . The interpretation is doubtful, if this

is the ordinary red-yellow transition then the transition pressure is displaced by an unusual amount by the shearing stress. It is not

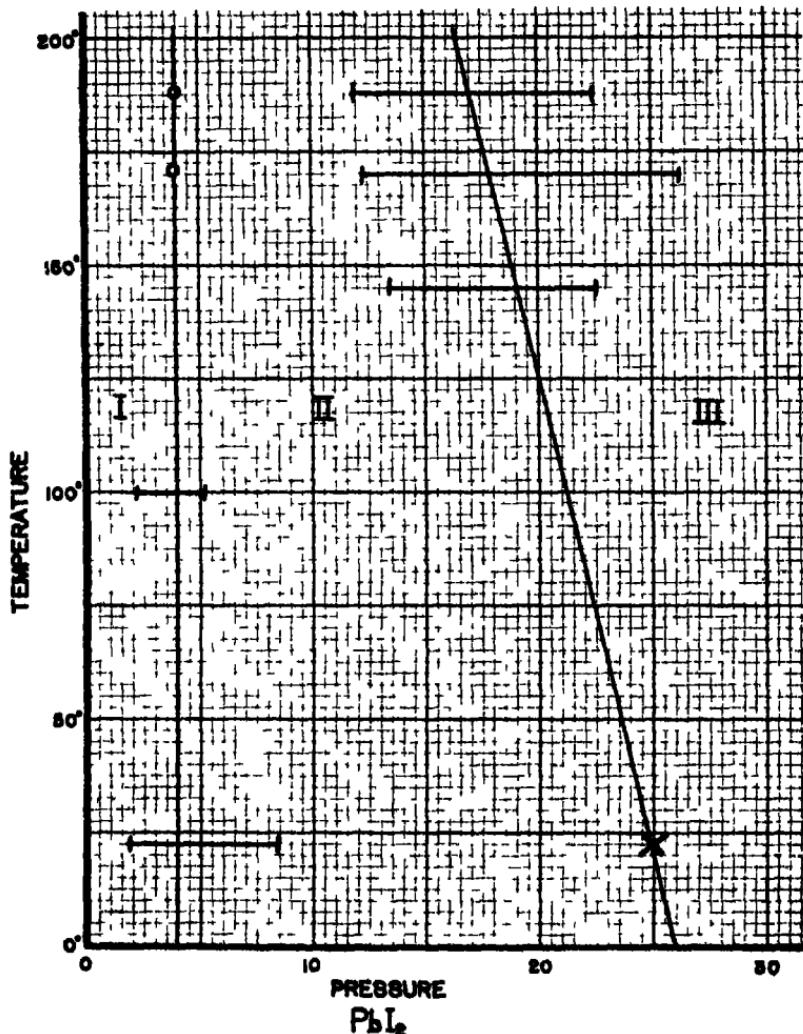


FIGURE 15 The phase diagram of  $\text{PbI}_2$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

unlikely that it is the transition found with the volume apparatus at  $146^\circ$ , the reason that it was not found with the volume apparatus

at room temperature must in this event be set down to too great sluggishness.

*Gel<sub>2</sub>*. This material I owe to the kindness of Professor K. T. Bainbridge, who in turn obtained it from Professor Albert W. Noyes, Jr. There was a sharp downward break of an unusual character in the shearing curve near 18,000 kg/cm<sup>2</sup>. In the volume apparatus the

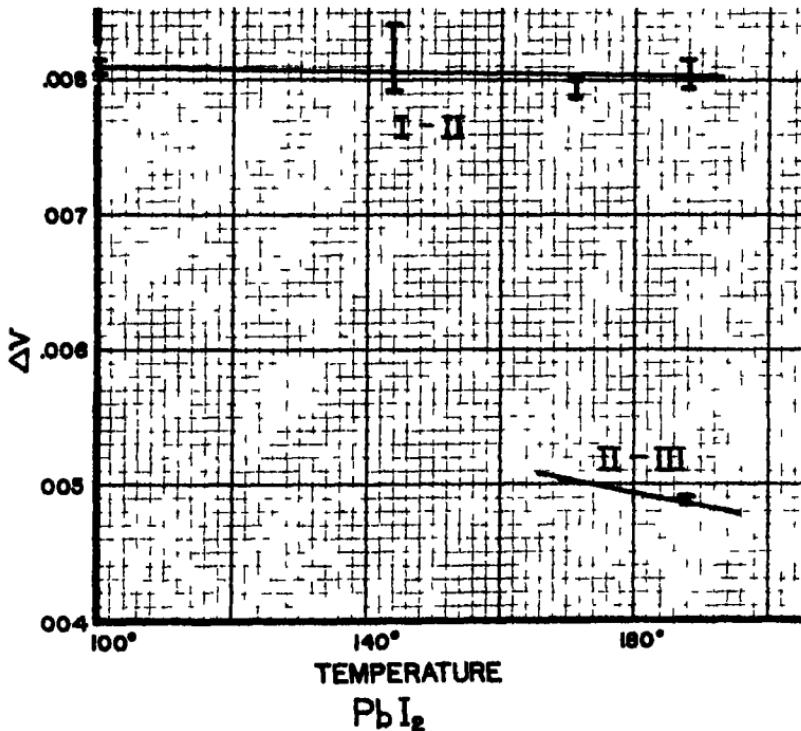


FIGURE 16 The volume change of the transitions of  $PbI_2$  in  $cm^3/gm$  against Centigrade temperature

first run with increasing pressure gave apparently a small discontinuity in volume at about 19,000. The reverse transition with decreasing pressure could not be definitely established, there was a definite break in direction of the piston displacement curve, but this occurred at the pressure where the stopper begins to move out of the collar, and the two effects could not be disentangled. A second run at room temperature, this time at 1,000 kg pressure intervals and four minute

time intervals, gave results more irregular than those of the first run, but not inconsistent with them. At 150° a somewhat smaller volume discontinuity was found at 29,000. On the whole the probabilities favor a transition at the pressures stated, with a volume discontinuity of the order of 0.0001 cm<sup>3</sup>/gm.

*PbI<sub>2</sub>*. This was "c p" stock from Eimer and Amend. The crystal structure is hexagonal, of the CdI<sub>2</sub> type. The shearing measurements showed a definite, but not striking, upward break at 26,000 kg/cm<sup>2</sup>, suggesting a transition. In the volume apparatus seven different runs were made, with a single filling and no accident. There are two new modifications, each with a comfortably large volume change. The transition which occurs at the higher pressure runs with practical velocity only at the higher temperatures, at 144° it had become so sluggish as to be difficult, and it could not be detected at all at room temperature. This is without doubt the transition found with the shearing apparatus, we have here another example of the effectiveness of shearing distortion in overcoming internal viscosity. The other transition which runs at comparatively low pressures has so far lost its sluggishness at the three highest temperatures that the width of the band of indifference vanishes, but at 100° and especially at room temperature the band of indifference is important.

The phase diagram is shown in Figure 15, the volume change in Figure 16. It is evident that the band of indifference is so wide that any values assumed for  $d\tau/dp$  must be rather hypothetical. I have therefore not ventured to give a table of the parameters of the transition.

*Cr<sub>2</sub>O<sub>3</sub>*. The material was "c p" stock from Eimer and Amend. Ordinarily a substance with as high a melting point as this has would not have been tried, because transitions of such substances are usually impossibly sluggish in my temperature range. The shearing measurements however, had shown an unusually definite indication of a transition at room temperature in the neighborhood of 28,000 kg/cm<sup>2</sup>, the shearing curve at this point taking a small abrupt dip and then rising abnormally at a continually accelerating pace at higher pressures.

Careful explorations were made with the volume apparatus on the two minute schedule at 150° and 175°. Apparently there is a sluggish transition beginning at both these temperatures at 26,000 kg/cm<sup>2</sup> with increasing pressure and running over a pressure interval of 8,000 kg/cm<sup>2</sup>. The volume change is of the order of 0.0004 cm<sup>3</sup>/gm. However, the evidence with regard to this transition is not as satisfactory as could be desired, there was no sign of the transition with decreasing pressure, and in the pressure range of the suspected

transition the creep was no more rapid than outside the range. Neither of these points is decisive, however, and on the whole I believe the evidence favors the transition.

*KCN* This was fresh "c p" stock from Eimer and Amend. The shearing curve gave a very definite indication of a transition, having a sharp upward break in direction. This means that the high pressure phase has a higher shearing strength than the low pressure phase. The pressure of the break was 26,000 kg/cm<sup>2</sup>. With the volume apparatus eight different runs were made, with a single filling, without accident, from CO<sub>2</sub> temperature to 146°. The transition phenomena are rich, and three new modifications were found. The transitions mostly run rapidly, and in some cases with unusually large volume changes, so that equilibrium pressures could be read with both phases present, with the result that unusually satisfactory values were obtained. This is one of the few substances for which good values were obtained at CO<sub>2</sub> temperature. A transition was first picked up at this temperature, which ran so sharply that when correction was made for friction the width of the band of indifference proved to be zero. It was again found at room temperature, of course also running without appreciable band of indifference. At 75° the transition had split into two, each running without appreciable band of indifference, one of the transitions carrying most of the volume change. At 100° the expected transitions II-III and III-IV were found at high pressure, but on plotting the results it was evident that a new transition had put in its appearance at low pressures. Not enough readings were obtained to give the volume change of this new transition. Further measurements between 85° and 150° substantiated the existence of a transition at comparatively low pressures, of a quite different character from the others. This transition is sluggish, the sluggishness rapidly increasing with decreasing temperature, which is doubtless the reason that it was not found at room temperature. Furthermore, the coordinates found first at 100° do not fit at all with the other coordinates found later for the new low pressure transition, the only possible explanation is that the transition first found at 100° is of an absolutely unstable form. The relations are such that it must be the low pressure form that is unstable, so that it is to be anticipated that under proper conditions, including perhaps previous exposure to high pressure, an absolutely unstable form can be realized at atmospheric pressure.

The experimental points are shown in Figures 17 and 18, and the transition parameters are given in Table VI. The parameters for the transition I-II are very rough, the best of them is probably  $\Delta v$ .

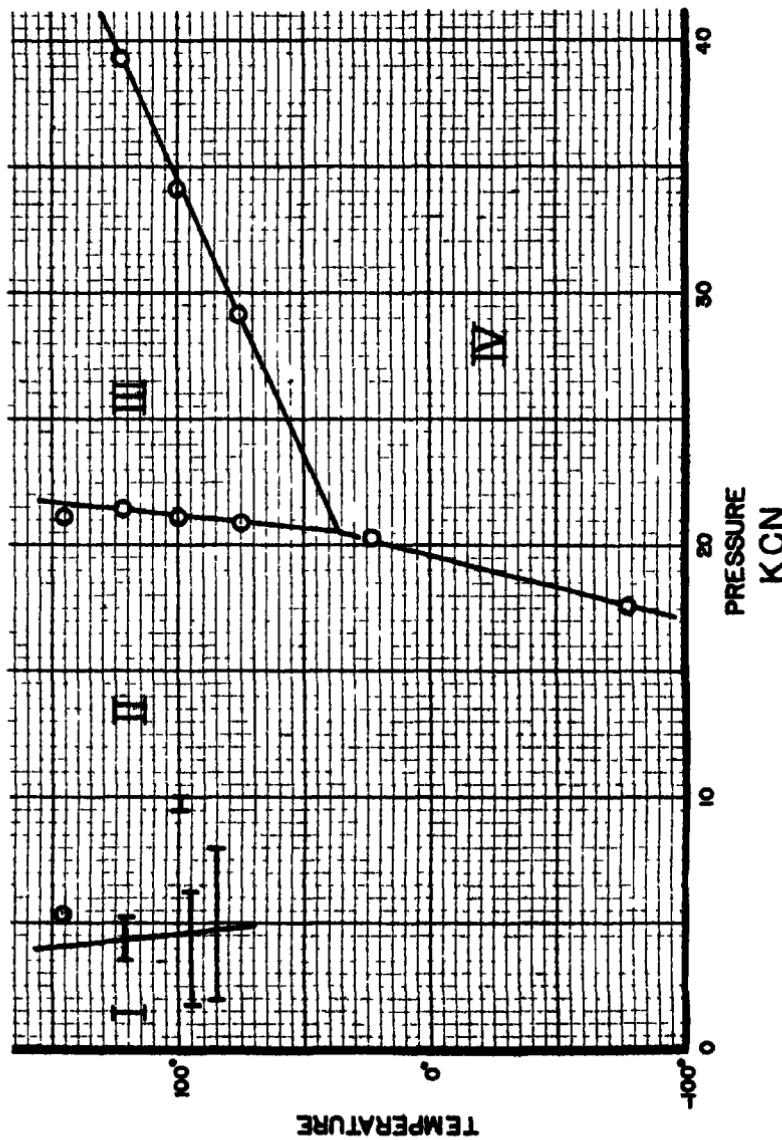


FIGURE 17 The phase diagram of KCN, Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>

TABLE VI  
TRANSITION PARAMETERS OF KCN

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Heat gm cal/gm
I-II					
4,800	80	- 0875	0150	61	1 42
4,000	150	- 0875	0230	111	2 61
II-III					
20,660	50	0895	0553	199	4 67
21,220	100	0895	0530	221	5 18
21,780	150	0895	0507	239	5 62
II-IV					
17,700	-80	0417	0638	295	6 91
18,900	-30	0417	0620	361	8 46
20,100	+20	0417	0602	423	9 91
III-IV					
23,540	50	00461	0031	238	5 58
32,220	90	00461	0025	197	4 62
40,900	130	00461	0016	140	3 28
TRIPLE POINT II-III-IV					
20,500	36°	II-IV    0417	0595	441	10 36
		II-III    0895	0558	192	4 51
		III-IV    00461	0037	248	5 82

KCN is cubic, NaCl structure. The fact that the phase diagram is so much more complicated than that of any of the simple ionic compounds of this structure suggests that the CN radical may not continue to function as a single unit at high pressures.

*AgCN* The material was "c p" stock from Emmer and Amend. The shearing curve showed a gentle upward break at 17,000 kg/cm<sup>2</sup>, suggesting a transition. Four runs were made in the volume apparatus at CO<sub>2</sub> and room temperatures, 90°, and 147°, with a single filling and without accident. Although no transition was found at CO<sub>2</sub>, one was found at the three others. The volume change was so small that it was not possible to obtain readings on the two phase system, for when the transition started it ran to completion. The high pressure phase is distinctly less compressible than the low pressure phase. This results in considerable uncertainty in the change of volume when there is as wide a region of indifference as here. The change of volume is roughly 0.0002 cm<sup>3</sup>/gm, a greater degree of accuracy is not justified.

by the results. The experimental values of transition pressure and temperature are shown in Figure 19. Sufficiently accurate values

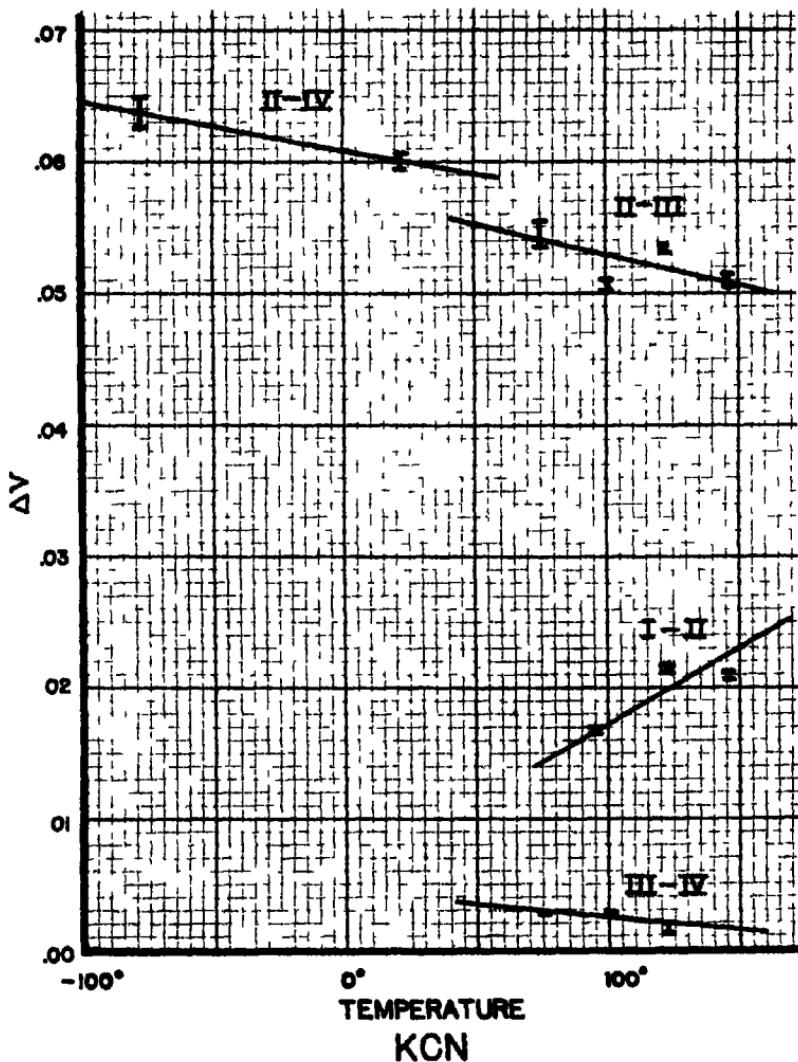


FIGURE 18. The volume change of the transitions of KCN in  $\text{cm}^3/\text{gm}$  against Centigrade temperature.

of the transition parameters can be taken from the figure, so that a table is not necessary.

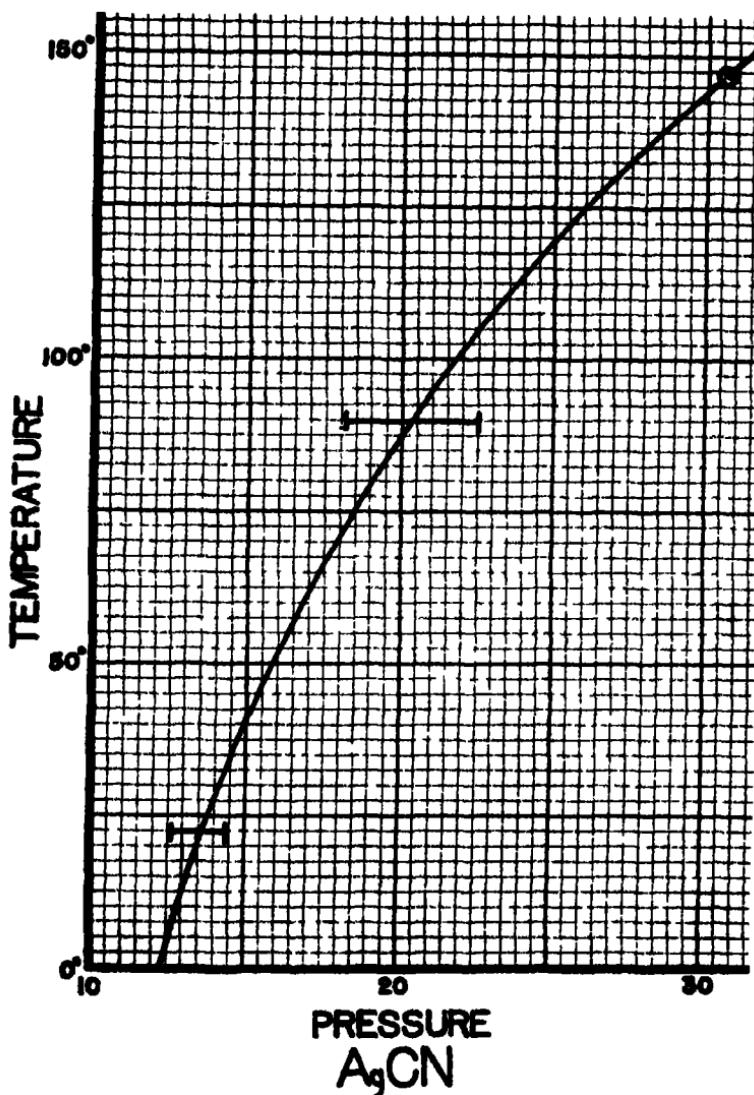


FIGURE 19 The transition line of AgCN, Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>

$\text{AgCN}$  is ortho-rhombic in structure, entirely unlike  $\text{KCN}$  so the great dissimilarity in phase diagrams is not surprising.

$\text{NaNO}_2$ . The shearing curve suggested a transition because it takes a gentle upward bend in the neighborhood of 15,000. Five different runs were made in the volume apparatus with two set-ups, one

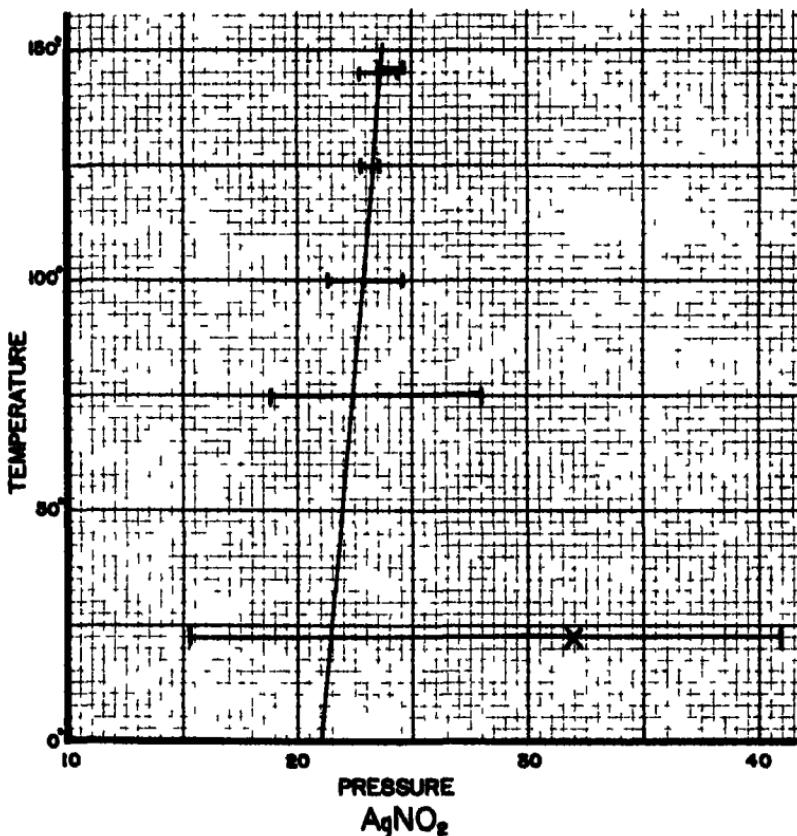


FIGURE 20. The transition line of  $\text{AgNO}_2$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$ . The cross shows the point of discontinuity on the shearing curve.

terminated by an explosion. Explorations were made at  $\text{CO}_2$  and room temperatures and  $150^\circ$ . No definite volume discontinuities could be found, but there were very sharp breaks in the direction of the curves at  $150^\circ$ . These breaks were obtained on both runs, were

found with increasing and decreasing pressure at approximately the same place, and could not well have been frictional effects on the outside of the stopper, as shown by a plot of the displacement of the stopper into the collar against pressure. At the other temperatures similar effects were found but less definite. It is probable that there is a transition with very small volume change, the high pressure phase being less compressible than the low pressure phase by approximately  $5.0 \times 10^{-7}$  (in  $\text{kg}/\text{cm}^2$  units and assuming 2.25 for the density). The transition pressure probably rises with temperature. If the somewhat

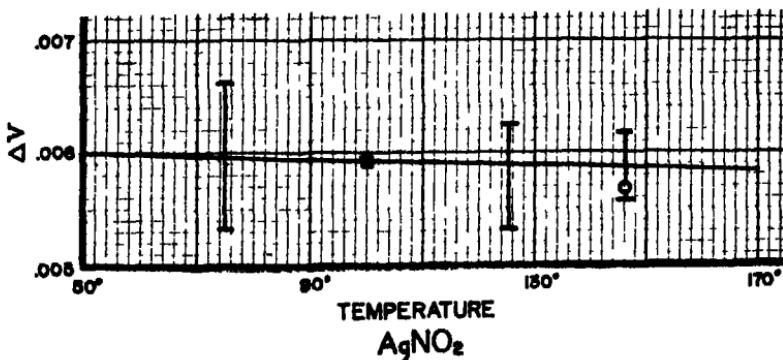


FIGURE 21. The volume change of the transition of  $\text{AgNO}_2$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature.

doubtful indications at  $-80^\circ$  are taken at their face value, the transition curve rises from  $6,000 \text{ kg}/\text{cm}^2$  at  $-80^\circ$  to  $17,000 \text{ kg}/\text{cm}^2$  at  $150^\circ$ .

$\text{KNO}_2$  has a transition with a transition line already studied<sup>9</sup> of somewhat the same general character as that just suggested for  $\text{NaNO}_2$ , but running at pressures of the order of  $5,000 \text{ kg}/\text{cm}^2$  lower. The volume change for  $\text{KNO}_2$  is fairly large. The crystal system of  $\text{NaNO}_2$  is ortho-rhombic, that of  $\text{KNO}_2$  has apparently not been determined.

$\text{AgNO}_2$ . The material was "c p" stock from Eimer and Amend. The shearing curve had given unusually clear indications of a transition, there being a large and sharp upward break at  $33,000 \text{ kg}/\text{cm}^2$ , which means that the high pressure modification has the higher shearing strength. Seven different runs were made in the volume apparatus at temperatures from  $-80^\circ$  to  $150^\circ$ , with a single filling and without mishap. There is a transition which rapidly becomes

sluggish at low temperatures, no trace was found of it at  $-80^\circ$ , and only doubtful indications at room temperature. At  $115^\circ$  and  $150^\circ$ , on the other hand, the transition ran sharply, approximately the same equilibrium pressure being approached from above and below.

The experimental results are shown in Figures 20 and 21, and the transition parameters in Table VII.

TABLE VII

TRANSITION PARAMETERS OF  $\text{AgNO}_3$ 

Pressure kg/cm <sup>2</sup>	Temperature $^{\circ}\text{C}$	$\frac{dt}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
21,000	0	0.556	0.0607	29.8	70
21,900	50	0.556	0.0600	34.8	82
22,800	100	0.556	0.0593	39.7	93
23,700	150	0.556	0.0586	44.5	1.09

The high pressure modification is markedly less compressible than the low pressure form, the difference being of the order of  $5 \times 10^{-6}$ , assuming 2.5 for the density.

$\text{RbNO}_3$ . This material was obtained from Mackay. The shearing measurements showed a smooth curve, with no suggestion of a transition.

$\text{RbNO}_3$  is known to be polymorphic at atmospheric pressure, there being three modifications and two transition points at  $164^\circ$  and  $219^\circ$ . I have previously<sup>10</sup> studied the transition line starting at  $164^\circ$ , it rises with pressure to  $218.6^\circ$  at 6,000 kg/cm<sup>2</sup>, and with a volume change falling from 0.0069 cm<sup>3</sup>/gm at atmospheric to 0.0043 at 6,000 kg/cm<sup>2</sup>.

One new modification was found in the higher pressure range. The volume change is considerably less than that of the transition previously measured, and it was not possible to set exactly on equilibrium. The transition is very sluggish, with a wide region of indifference, at the lower temperatures, but at the two highest temperatures the region of indifference becomes vanishingly small. The sluggishness at the lower temperatures was so great that measurements of the change of volume were not possible there. Even at the higher temperatures the changes of volume could be determined with much less accuracy than usual.

The experimental results are shown in Figures 22 and 23, and the thermodynamic parameters are collected in Table VIII. There is considerable uncertainty in the slope of the transition line, it may well have curvature in abnormal direction. The general trend of the transition line is to rise more rapidly than the line already studied, so

that a triple point at considerably higher temperatures may be suspected.

TABLE VIII  
TRANSITION PARAMETERS OF RbNO<sub>3</sub>

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
16,500	0	0211	0017	22 0	0 54
18,900	50	0211	0021	32 2	0 79
21,300	100	0211	0025	44 2	1 08
23,700	150	0211	0029	58 2	1 42
26,000	200	0211	0033	74 1	1 82

*CsNO<sub>3</sub>* I am indebted for this material to Professor G P Baxter, it was of exceptional purity. The shearing measurements gave a smooth curve, with no hint of a transition.

This substance has a known transition at atmospheric pressure at 154°, and in my previous work the effect of pressure on the transition was studied up to 6,000 kg/cm<sup>2</sup> and 207°<sup>10</sup>. In the present work examination was made for other transitions to 50,000 kg/cm<sup>2</sup> at room temperature, 125°, 150°, and 175°. Nothing new was found at room temperature, but at the three higher temperatures there is fairly certain evidence of a transition with very small change of volume at pressures between 25,000 and 30,000. In addition to this new transition, the transition formerly studied was picked up at the lowest end of the pressure range at 175°, but no attempt was made to redetermine the parameters.

The experimental values for the transition pressures are shown in Figure 24. The change of volume is of the order of 0 00015 cm<sup>3</sup>/gm, with a large degree of uncertainty. In view of the uncertainty of the results it did not seem worth while to attempt to calculate the other parameters of the transition.

*AgNO<sub>3</sub>* The material was old "c p" stock from Merck. This substance has already been studied up to 12,000 kg/cm<sup>2</sup><sup>10</sup>. There is a transition at atmospheric pressure at about 160° of the ice type, the transition line runs downward, reaching 7,000 kg/cm<sup>2</sup> at 100°, not far beyond this the transition line experiences an abnormally large downward curvature such that at 0° C the pressure has risen to only 9,800 kg/cm<sup>2</sup>. The curvature and various irregularities in the change of volume raised the suspicion at the time of the early work that there might be other modifications, but I was not successful in finding any.

The shearing measurements gave a curve for room temperature with a very pronounced upward break at about 16,000, and smooth beyond the break up to 50,000. The break was interpreted as due to the known transition.

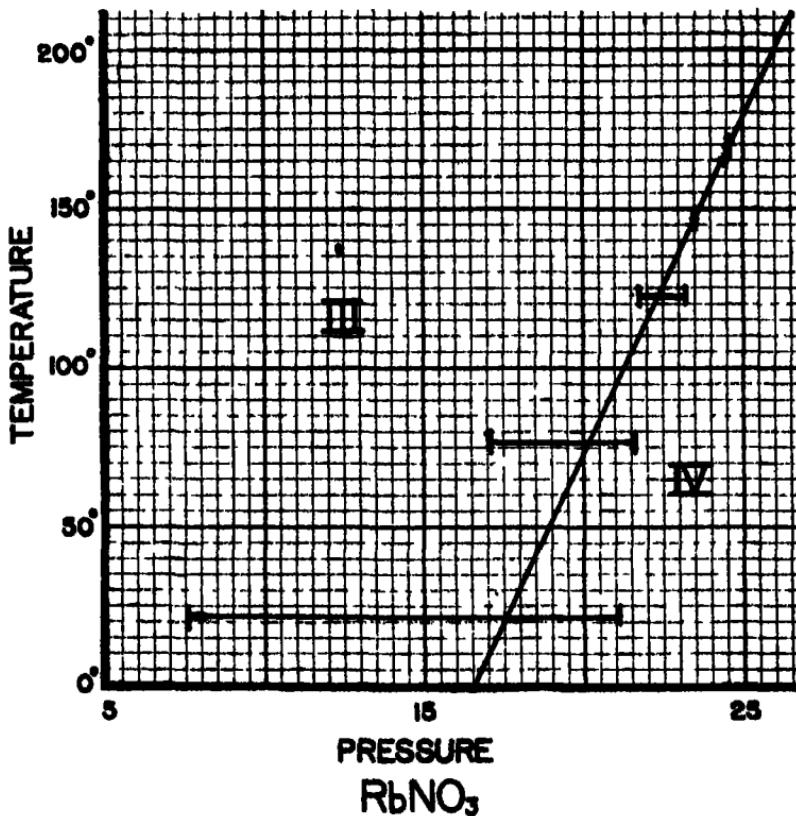


FIGURE 22. The high pressure transition line of  $\text{RbNO}_3$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$ .

The first study with the volume apparatus was made at solid  $\text{CO}_2$  temperature, the object being to find whether the great curvature just above  $0^\circ \text{ C}$  continues to lower temperatures. It was anticipated that the transition would be difficult to locate because the majority of transitions become impractically sluggish at this temperature, and in particular the transition was rapidly becoming more sluggish when last studied at  $0^\circ \text{ C}$ . The transition was found, but it was not par-

ticularly sluggish, so that the equilibrium pressure could be shut within fairly narrow limits. Furthermore the pressure was higher than anticipated, so that the transition line already known would have to reverse its direction in order to reach the new point, and the change of volume was also considerably larger than expected. Unfortunately the apparatus was taken down before the significance of these results was appreciated, the probable interpretation, of course, being that there must be another modification. The apparatus was

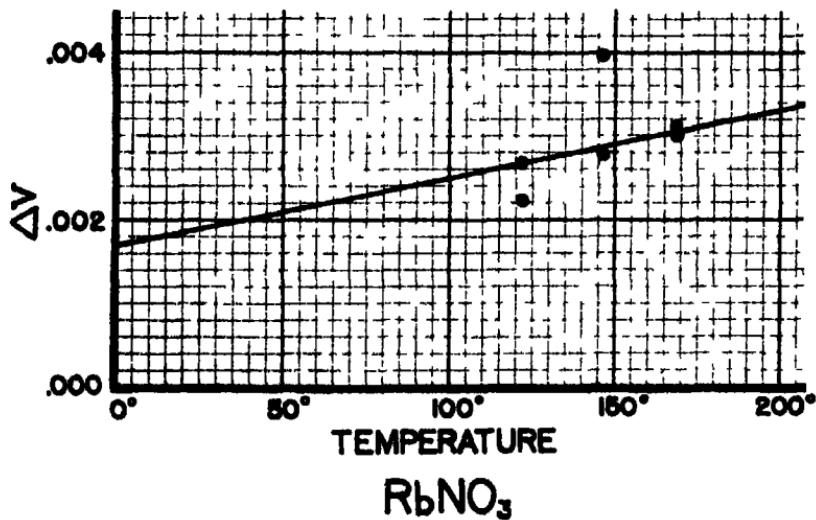


FIGURE 23 The volume change of the high pressure transition of  $\text{RbNO}_3$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

then set up again and measurements made at higher temperatures. There did indeed turn out to be other modifications, two at least with comfortably large volume changes, running at pressures beyond 30,000. The transition lines run fairly nearly vertically, and so close together that some care is necessary to disentangle them.

The transition III-IV with the largest volume change, about 5 per cent, occurs at pressures near 40,000. Considerable super-pressure is necessary to start the transition, the result is that changes of volume for this transition could be measured only with decreasing pressure. With increasing pressure approximately 50,000 is necessary to start the transition at room temperature and at 50,000 there is appreciable creep in the apparatus. At higher temperatures it is

true the pressure of the transition becomes somewhat lower and the amount of super-pressure less, but at the same time creep occurs at lower pressures, so that the net result was that at no temperature could creep be disentangled from the legitimate volume change with increasing pressure. The volume change was large enough, however, so that there was no difficulty in establishing the pressure of the transition with increasing pressure as well as with decreasing pressure.

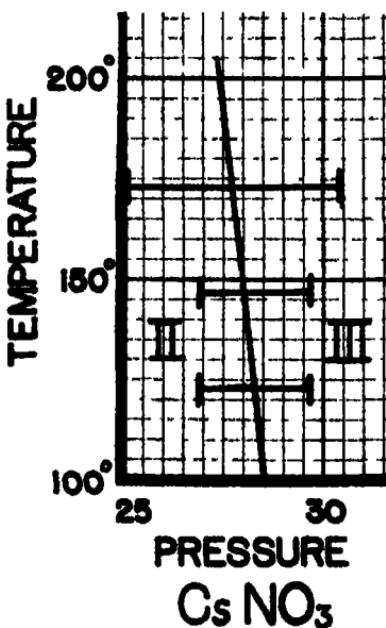


FIGURE 24 The high pressure transition line of  $\text{CsNO}_3$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

The other high pressure transition, II-III, has a volume change of the order of only a third of that of III-IV, but it is still large enough to be comfortably measurable except for the fact that the pressure of the transition is so near to that of III-IV that it is not easy to separate completely the two transitions. At first measurements were made successively on the two transitions, but this was not particularly satisfactory, and the transition II-III was finally studied by itself, taking care not to raise the pressure high enough to start the transition to IV. The sluggishness of the transition II-III rapidly becomes greater at lower temperature, this made impractical the

isolated measurement of II-III below 50° C. At the higher temperatures the sluggishness disappears, while that of III-IV does not, thus made it feasible to follow the transition II-III to somewhat higher temperatures than III-IV.

At the higher temperatures, where the transitions run rapidly, the results were clean cut and satisfactory. At lower temperatures, that is, 50° or less, the situation is much less clear. On at least three occasions at room temperature and 50° irregularities were found larger than the usual experimental error, but not certainly larger than possible error, which strongly suggested other transitions. These effects could not be repeated. This, however, is not definite evidence. Phenomena of suppression and transgression may be particularly prominent with  $\text{AgNO}_3$ . Thus on one occasion the modification II was held at room temperature at approximately 20,000 kg/cm<sup>2</sup> for 42 hours. It had then apparently lost the capacity to change to either of the high pressure modifications, two excursions to the maximum pressure at 60° not giving any transition at all. The ability to change to III and IV was restored at 120°. It is almost certain that there must be other transitions at lower temperatures. The location of the transition at solid  $\text{CO}_2$  temperature is itself strong presumptive evidence for this, because abnormal curvature would be demanded of either the I-II or the II-III line to reach this point. In addition, there is the change of volume, which is too large for either I-II or II-III. But perhaps the most convincing evidence is the velocity of the transition, which was unexpectedly large, certainly very much larger than could be expected by any extrapolation from the results on the line II-III. On the other hand, there are irregularities in the transition velocity on the line I-II pointing to something more complicated. Figure 25 shows that the width of the region of indifference is greater at room temperature than at 50°. In my previous work abnormal variations were found in the transition velocity near 0°. In Figure 25 the small circles indicate the coordinates of I-II previously found. There is failure of agreement at the lower temperatures. All things considered it seems to me that the most probable interpretation is that there are at least two new modifications with transition lines running somewhere in the region suggested by the dotted lines in Figure 25. The change of volume must be almost all carried by the transitions meeting near  $\text{CO}_2$  temperature, because the measured change of volume at this point is approximately the sum of I-II and II-III. In addition to the transitions indicated, it is not altogether unlikely that there may be a transition with very small change of volume and approximately

horizontal transition line running across the II region of the diagram between room temperature and  $60^{\circ}$ . Further experimental study

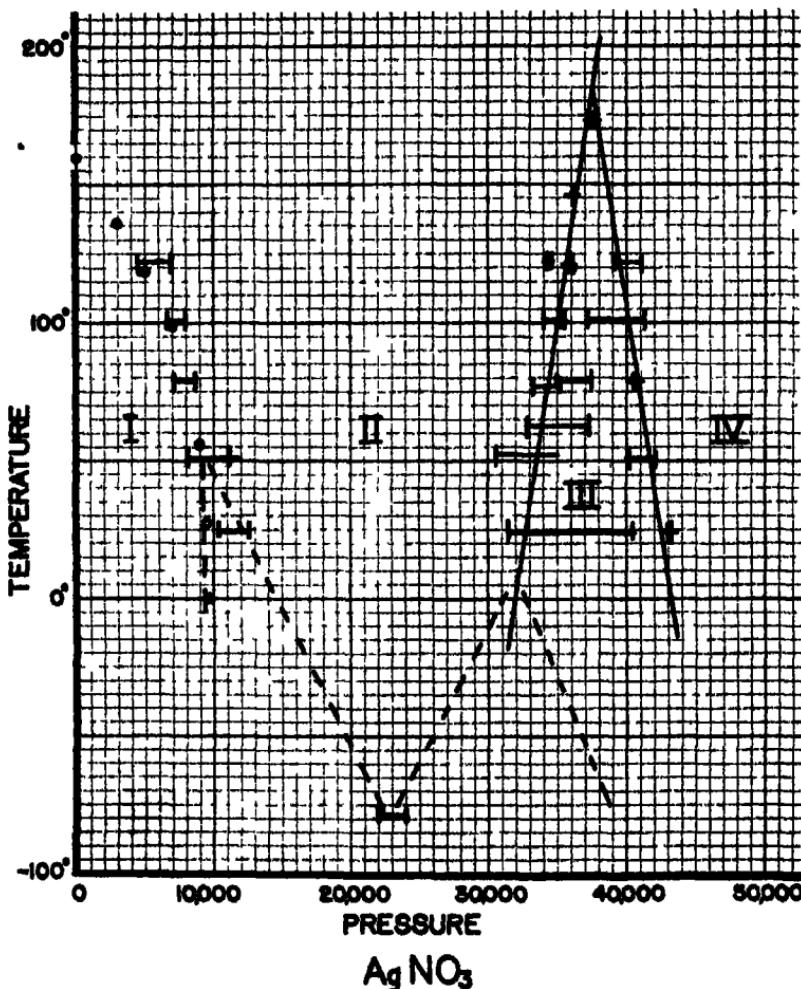


FIGURE 25 The phase diagram of AgNO<sub>3</sub>, Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>. The circles show the previously determined coordinates, and the dotted lines suspected new transitions

of the questions raised here would demand a considerable modification in the apparatus in order to permit the control of temperatures between room temperature and the CO<sub>2</sub> point

The results are shown in Figures 25 and 26, and the values of the transition parameters that can be established with confidence in Table IX. The data for I-II have been given in the previous paper,

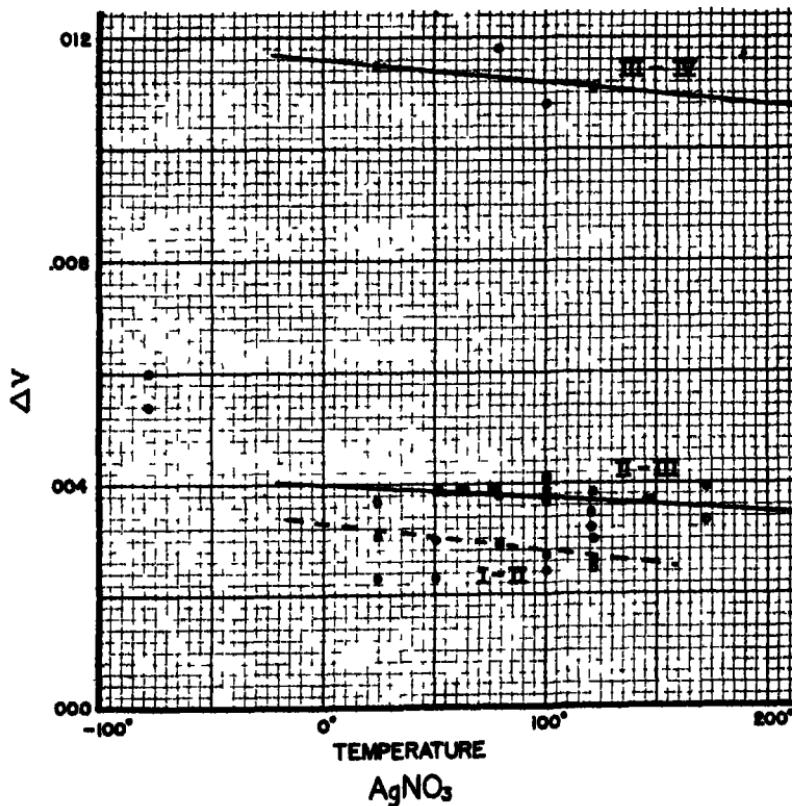


FIGURE 26 The volume change of the transitions of  $\text{AgNO}_3$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

and are doubtless more accurate than those found here, which are sufficiently well reproduced in the figures

TABLE IX

TRANSITION PARAMETERS OF AgNO<sub>3</sub>

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
II-III					
32,000	0	0.333	0.0400	32.8	0.77
33,500	50	0.333	0.0388	37.7	0.88
35,000	100	0.333	0.0375	42.0	0.98
36,500	150	0.333	0.0363	46.1	1.08
38,000	200	0.333	0.0350	49.7	1.17
III-IV					
43,200	0	- 0.333	0.116	95	2.23
41,700	50	- 0.333	0.114	111	2.60
40,200	100	- 0.333	0.112	126	2.94
38,700	150	- 0.333	0.110	140	3.27
37,200	200	- 0.333	0.108	153	3.60

*NaClO<sub>3</sub>*. The shearing curve of this substance has an abrupt drop in the neighborhood of 39,000, suggesting a transition. Nine different runs were made with the volume apparatus, all with one filling and without accident, at various temperatures from -80° to 170°. There are three new high pressure modifications, the phase diagram is not unlike that of KCN.

The experimental points are shown in Figures 27 and 28, and the transition parameters in Table X. The parameters given are in some cases rather rough, and must not be extrapolated beyond the limits given. For example, if the difference of volume between II and III were extrapolated linearly with temperature it would change sign in the neighborhood of 50°, an absurd result. The actual curves for  $\Delta\tau$  must depart considerably from linearity, as do probably also the pressure-temperature curves.

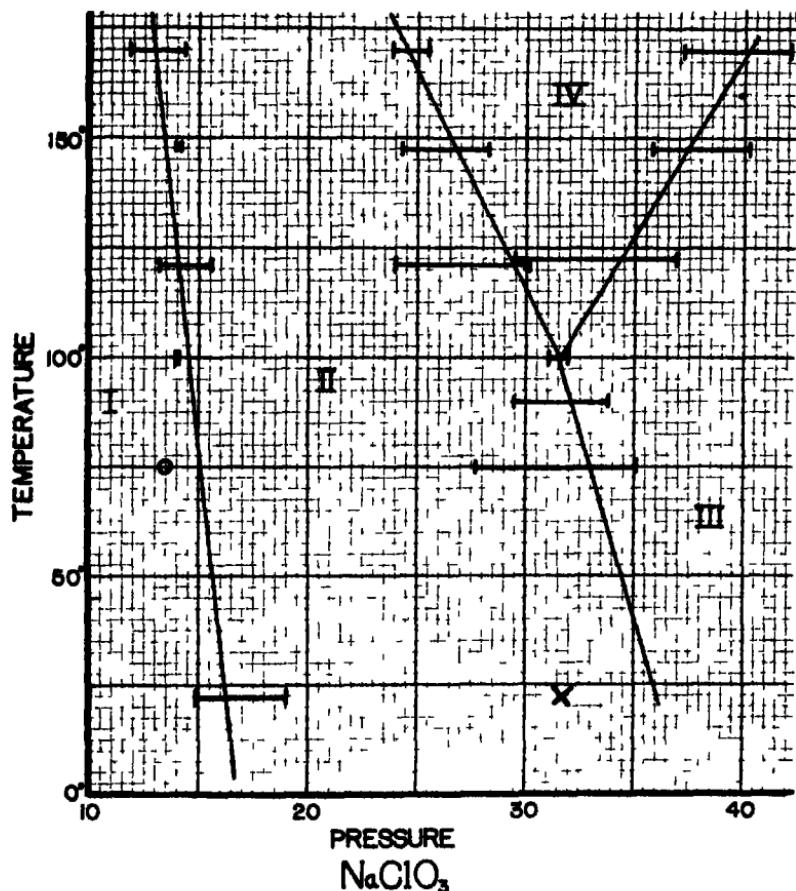


FIGURE 27 The phase diagram of  $\text{NaClO}_3$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

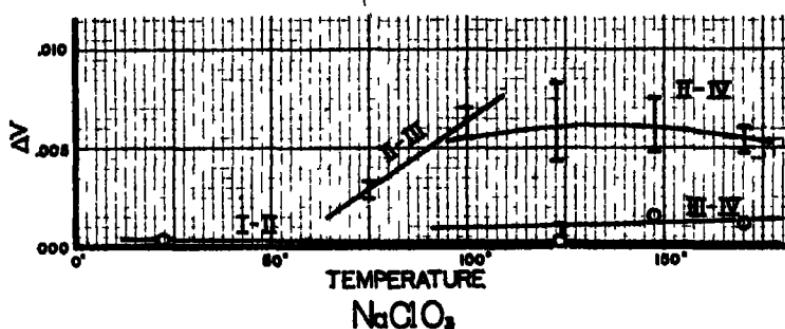


FIGURE 28 The volume change of the transitions of  $\text{NaClO}_3$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

TABLE X

TRANSITION PARAMETERS OF  $\text{NaClO}_3$

Pressure $\text{kg}/\text{cm}^2$	Temperature $^\circ\text{C}$	$\frac{d\tau}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	Latent Heat $\text{gm cal/gm}$
I-II					
16,300	20	- 0455	00035	2 25	053
15,200	70	- 0455	00028	2 11	050
14,100	120	- 0455	00020	1 73	041
13,000	170	- 0455	00018	1 26	030
II-III					
33,100	75	- 0157	0030	66	1 56
31,500	100	- 0157	0065	154	3 02
II-IV					
31,500	100	- 0102	0055	201	4 71
28,070	135	- 0102	0061	250	5 86
24,640	170	- 0102	0055	239	5 60
III-IV					
31,500	100	+ 00796	- 0010	46 9	1 10
35,900	135	+ 00796	0012	63 0	1 47
40,290	170	+ 00796	0014	77 9	1 83
TRIPLE POINT II-III-IV					
31,500	100	II-IV	- 0102	0055	201
		III-IV	+ 00796	- 0010	47
		II-III	- 0157	0065	1 54

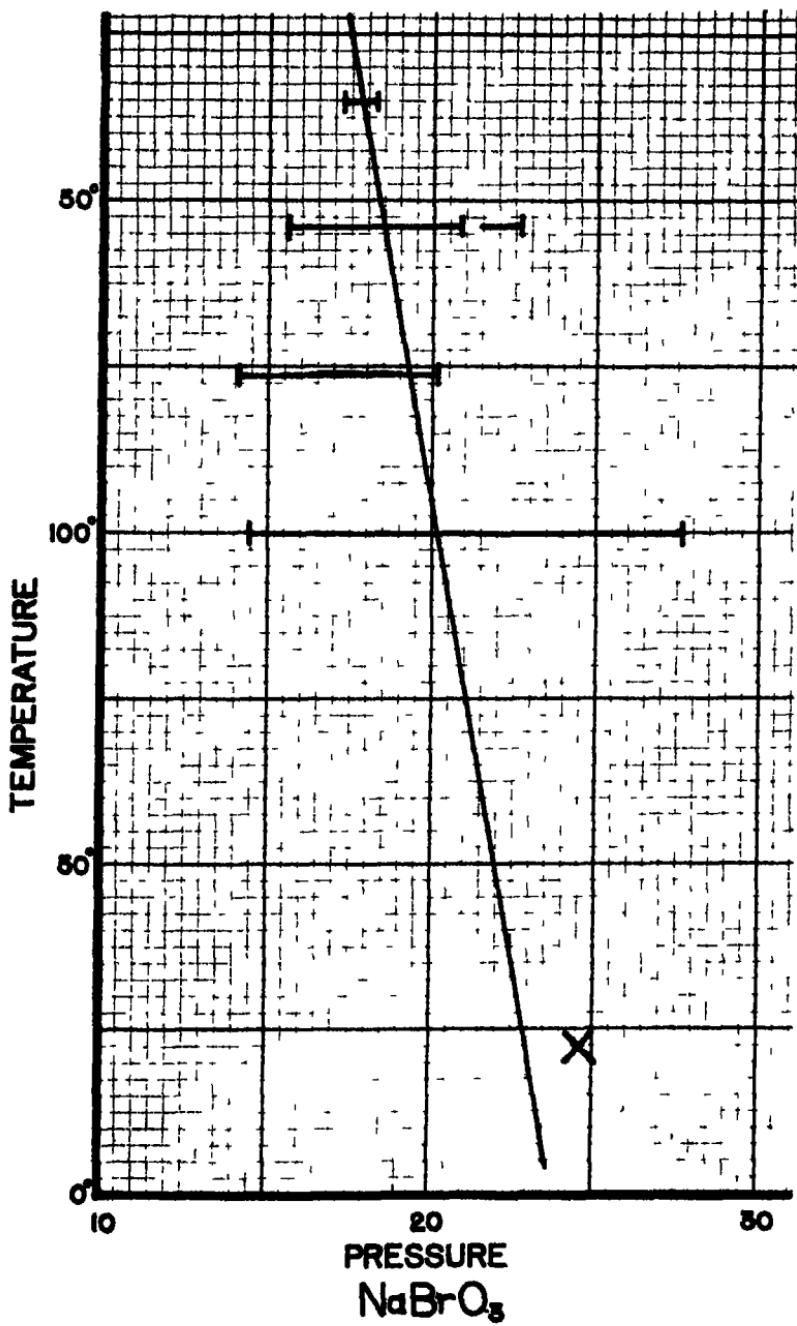


FIGURE 29 The transition of  $\text{NaBrO}_3$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

The triple point II-III-IV affords an interesting example of the way in which the speed of a transition increases and the width of the band of indifference decreases as the triple point temperature is approached from below. Figure 27 shows how the band of indifference between II and III has almost vanished at the triple point temperature, whereas at a temperature only a few degrees higher, where the transitions II-IV and IV-III replace II-III the transitions have again become sluggish, with wide band of indifference, which becomes less as temperature rises.

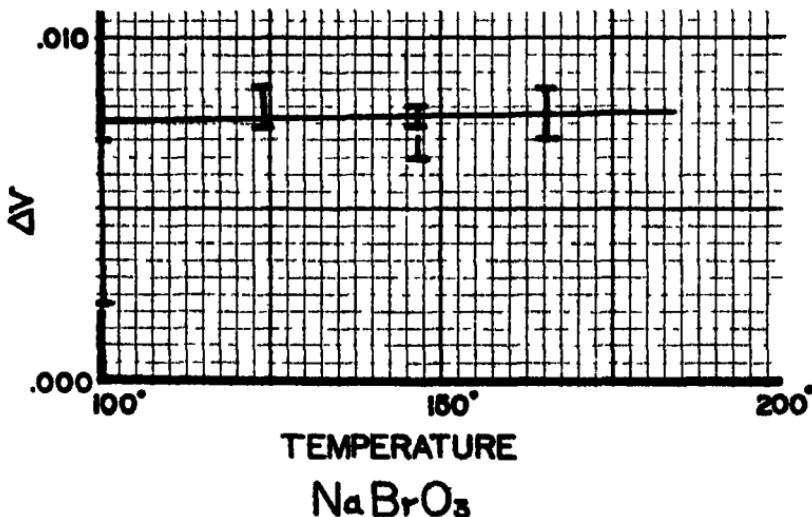


FIGURE 30 The volume change of the transition of  $\text{NaBrO}_3$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature.

$\text{NaBrO}_3$ . This was "c p" stock from Eimer and Amend. The shearing curve has a rather sharp knee at 26,000, at which the character of plastic flow abruptly changes from noisy and snapping to quiet. A transition might be suspected at such a point, but other cases have been found of similar behavior in shear with no transition.

The measurements in the volume apparatus disclosed one new high pressure form with a rather large change of volume. Seven different runs were made from  $\text{CO}_2$  temperature to  $170^\circ$ , with two different fillings of the apparatus. Measurements with the first filling were terminated by an explosion. The transition has a high temperature coefficient of activity; at  $\text{CO}_2$  and room temperatures it is so sluggish

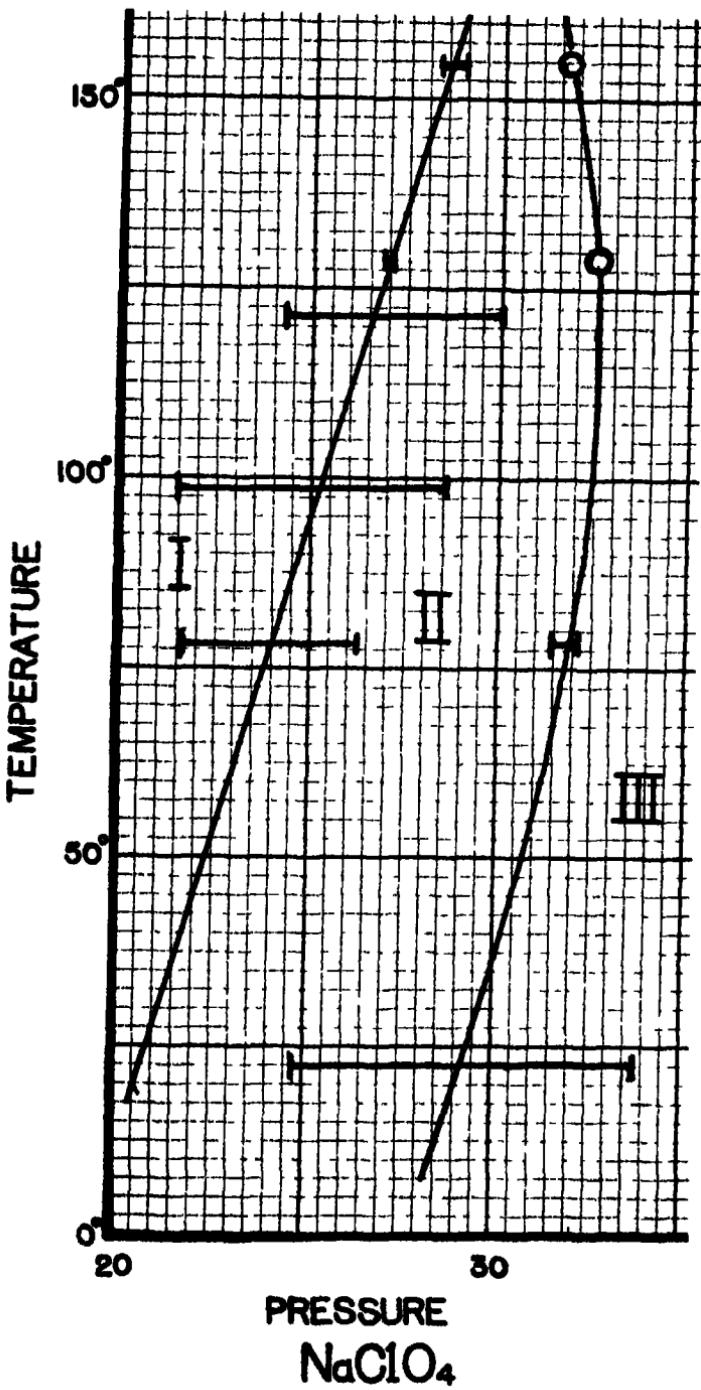


FIGURE 31 The phase diagram of  $\text{NaClO}_4$ , Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>

that nothing definite could be established. At 100° the width of the band of indifference is about 16,000 kg/cm<sup>2</sup>, above 100° the width becomes less, nearly vanishing at 170°.

The experimental values are shown in Figures 29 and 30, and the parameters in Table XI. It is obvious from the figure that both transition curve and change of volume have considerable uncertainty.

TABLE XI  
TRANSITION PARAMETERS OF NaBrO<sub>3</sub>

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
20,200	100	- 027	0076	105	2 4
18,900	135	- 027	0077	116	2 7
17,600	170	- 027	0078	128	3 0

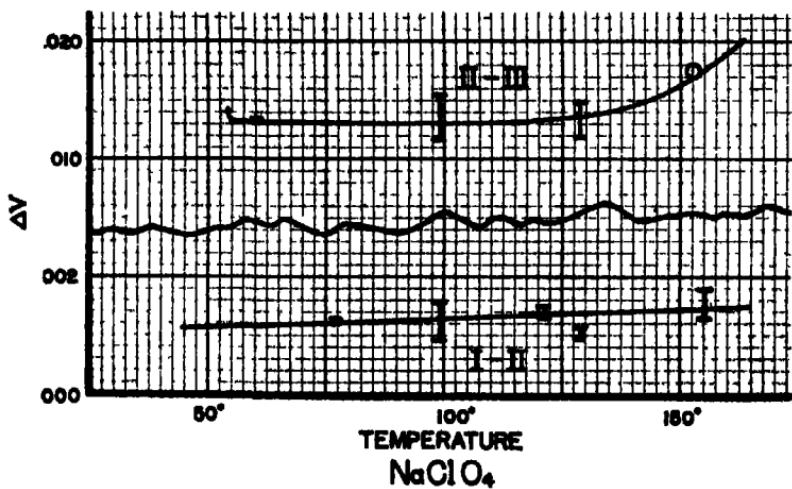


FIGURE 32 The volume change of the transitions of NaClO<sub>4</sub> in cm<sup>3</sup>/gm against Centigrade temperature. Notice the change of scale for the two transitions.

NaClO<sub>4</sub>. The material was "c p" stock from Eimer and Amend. The shearing curve had one inconspicuous upward break at 37,000, and another exceptional point at 25,000 where the character of the plastic flow changed from smooth to scratchy, but without noticeable change in slope, so that perhaps two transitions would be suggested, although one would not have felt great confidence in this prediction. Two new phases were as a matter of fact found with the volume

apparatus Seven runs were made in all with a single filling, without accident, in the temperature range from  $-80^{\circ}$  to  $155^{\circ}$

The experimental results for transitions curves and change of volume are shown in Figures 31 and 32, and the calculated transition parameters in Table XII. The high pressure transition II-III runs readily at the higher temperatures, and with so large a change of volume that equilibrium readings could be obtained with both phases present. There seems to be no question but that the transition line II-III deviates markedly from linearity.

TABLE XII  
TRANSITION PARAMETERS OF  $\text{NaClO}_4$

Pressure $\text{kg/cm}^2$	Temperature $^{\circ}\text{C}$	$\frac{d\tau}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	gm cal/gm
I-II					
22,300	50	0167	00115	22 3	52
25,300	100	0167	00182	29 5	69
28,300	150	0167	00148	37 5	88
II-III					
29,000	20	0182			
31,000	60	0227	0134	197	4 6
32,500	100	0454	0131	108	2 5
32,600	130	— 0909	0136	— 60	— 1 4
31,500	160	— 0130	0190	— 633	— 14 8

In addition to the transitions given there is some very doubtful evidence for a transition with very small volume change in the region around  $150^{\circ}$  and  $10,000 \text{ kg/cm}^2$ .

$\text{NaIO}_4$ . This was obtained from Mackay. The shearing curve was normal enough, with no suggestion of a transition.

With the volume apparatus a small transition was found, of such characteristics that it is difficult to establish the parameters with any accuracy. Runs were made at room temperature,  $125^{\circ}$ , and  $150^{\circ}$ , with two different fillings of the apparatus. With increasing pressure the transition runs so sluggishly and with such small volume change that one could not be sure of even the existence of the transition. With decreasing pressure, however, there is an abrupt discontinuity of volume, but of such small magnitude that no equilibrium setting with both phases could be attempted. This discontinuity on decreasing pressure was definitely established at approximately the same pressure at each of three runs at  $125^{\circ}$ . At room temperature it was not found, because of too great sluggishness probably. At  $150^{\circ}$  fairly

good evidence of the discontinuity was also obtained, but with some uncertainty due to leak in the absolute gauge with which the hydraulic press was controlled. This was a new type of gauge under trial, and was used for this one run only.

The pressure of volume discontinuity with decreasing pressure was 9,000 kg/cm<sup>2</sup> at 125° and 25,000 at 150°. Since the transition with increasing pressure could not be located, it is not possible to guess how wide the region of indifference is and hence to estimate what the true equilibrium pressures are at these temperatures. It is probable, however, that the great difference between the two pressures just quoted cannot be entirely explained by variation of the width of the region of indifference in such a comparatively narrow temperature range, so that it is probable that the transition line runs more nearly horizontally than for most substances. A consequence of this would be that there should be a transition at atmospheric pressure in the neighborhood of 100°.

The volume discontinuity as measured was 0.0010 cm<sup>3</sup>/gm, consistently for all four measurements. It is not possible to tell how close this is to the volume change at the transition itself, since a difference of compressibility of the two phases, combined with the fact that the pressure of discontinuity may have been some distance from the true equilibrium pressure, would falsify the true change of volume. It is probable, however, that this falsification cannot be large because the discontinuity at 150° was so nearly the same as that at 125°, and that 0.0010 is not far from the true volume change of the transition.

In view of the uncertainty of the measurements I have not thought it worth while to give diagrams or tables in greater detail.

*KClO<sub>3</sub>.* This is already known to have a transition,<sup>11</sup> which has been studied to 12,000 kg/cm<sup>2</sup> with my previous apparatus between 0° and 200°. In the 50,000 apparatus explorations were made to the maximum at CO<sub>2</sub> temperature and 150°. At the lowest temperature the transition apparently starts at 13,000, and continues running all the way to 50,000, pressure being increased at the rate of 2,000 kg/cm<sup>2</sup> in four minutes. On release of pressure the reverse transition did not start until 1,600 was reached. At 150° the transition ran rapidly, within pressure limits of 700 kg/cm<sup>2</sup>. The mean transition pressure was 7,400 kg/cm<sup>2</sup> and the mean change of volume 0.027 cm<sup>3</sup>/gm, against my previous values at this temperature of 7,200, and 0.0248 cm<sup>3</sup>/gm respectively. No other transition was found up to 50,000. The shearing curve was normal with no indication of a transition.

$KIO_4$  The material was "c p" stock from Eimer and Amend. The shearing curve had a minor break downward at 17,000, which of

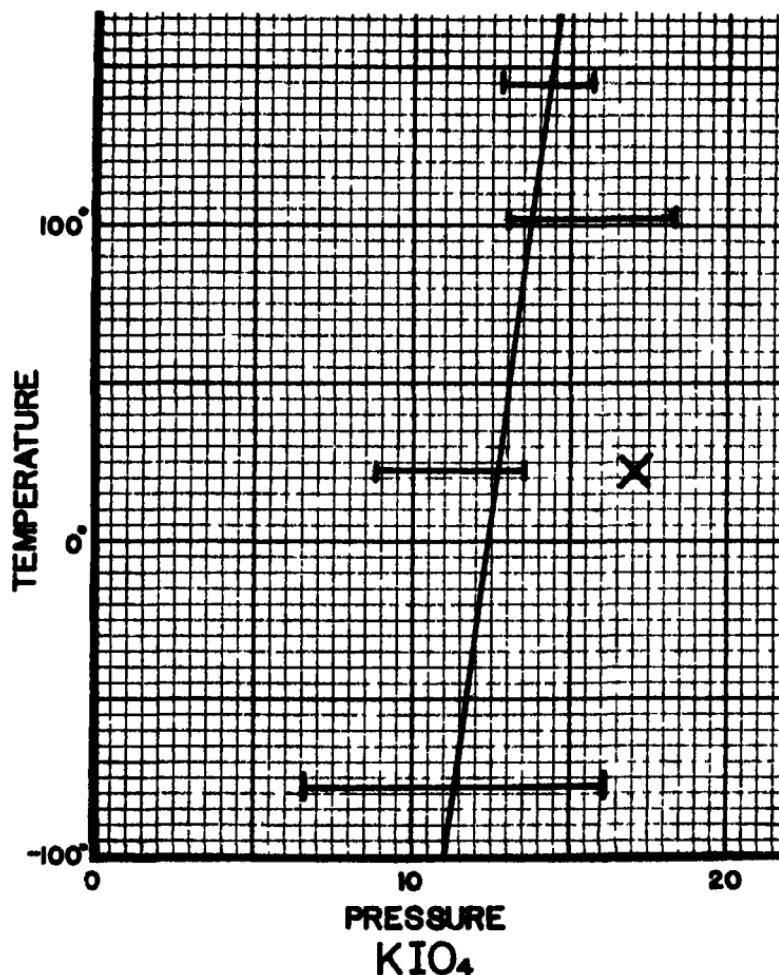


FIGURE 33 The transition line of  $KIO_4$ , Centigrade temperature against pressure in thousands of  $kg/cm^2$ . The cross indicates the point of discontinuity of the shearing curve.

itself would probably not have been enough to raise the suspicion of a transition. Four runs were made with the volume apparatus at

-80°, room temperature, 102°, and 145°, with a single filling and without accident. There is a transition running nearly vertically, with little latent heat, roughly at 12,000 kg/cm<sup>2</sup>. The volume change is not great enough to permit measurements on the two phase system, but once the transition had started, it always ran to completion. The transition is highly unsymmetrical, in that the volume change when

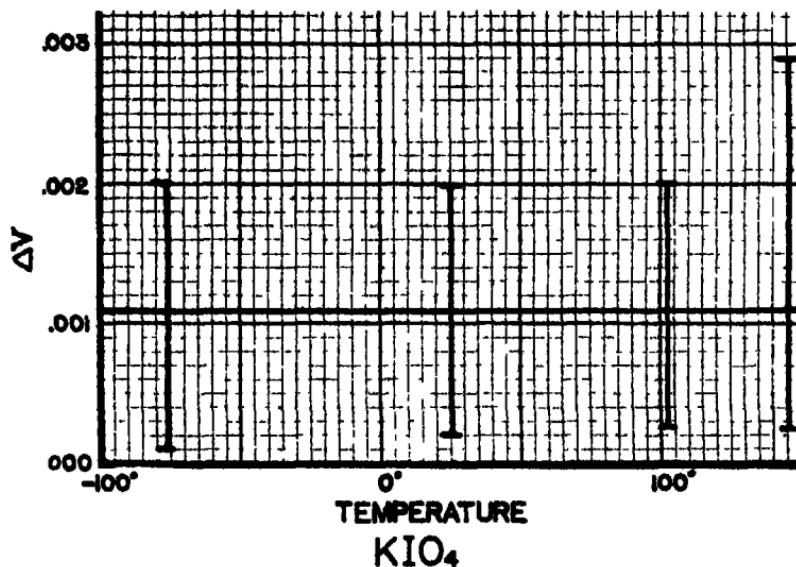


FIGURE 34. The volume change of the transition of KIO<sub>4</sub> in cm<sup>3</sup>/gm against Contigraide temperature

the transition runs with increasing pressure is always very much less than when it runs with decreasing pressure. This indicates that the high pressure form is less compressible than the low pressure form, the difference of compressibility is of the order of  $2 \times 10^{-7}$  (kg/cm<sup>2</sup> units)

The experimental results are shown in Figures 33 and 34, and the transition parameters in Table XIII

TABLE XIII  
TRANSITION PARAMETERS OF KIO<sub>4</sub>

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{dt}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
11,300	-80	074	0011	2 9	067
12,800	+35	074	0011	4 6	107
14,400	150	074	0011	6 3	148

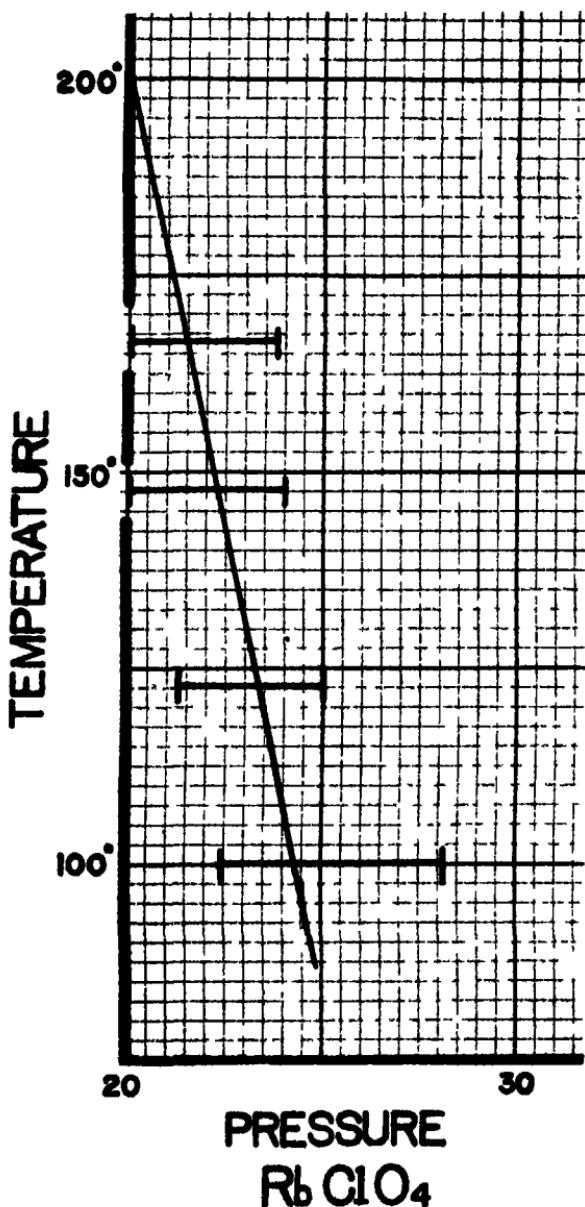


FIGURE 35 The transition line of RbClO<sub>4</sub>, Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>

$RbClO_4$ . This was obtained from MacKay, made from "c p" materials by the action of  $HClO_4$  on  $Rb_2SO_4$ . The shearing curve had a pronounced maximum at 24,000, and a minimum of about one half the maximum at 40,000. A transition is therefore to be confidently expected.

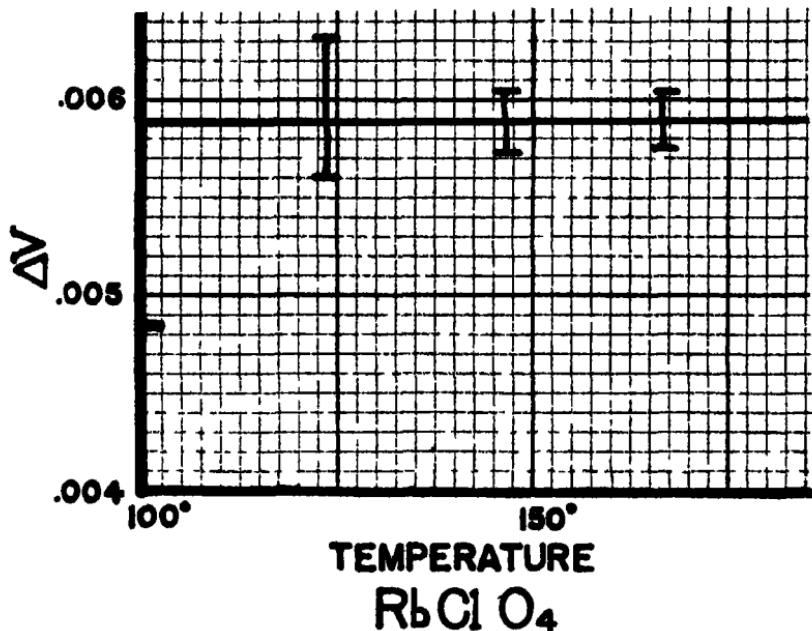


FIGURE 36. The volume change of the transition of  $RbClO_4$  in  $cm^3/gm$  against Centigrade temperature.

Five runs were made with the volume apparatus at temperatures from room temperature to 167° with a single filling of the apparatus without accident. Nothing was found at room temperature out to 50,000. The transition was definitely located at the other temperatures, however. Even at the highest temperatures it is somewhat sluggish, and since the change of volume is not large, it was not possible to obtain equilibrium readings on the two phase system. The experimental points are shown in Figures 35 and 36, and the transition parameters in Table XIV.  $RbClO_4$  is known to have a transition at atmospheric pressure at 279°, it seems highly probable that the high pressure modification found here must be new.

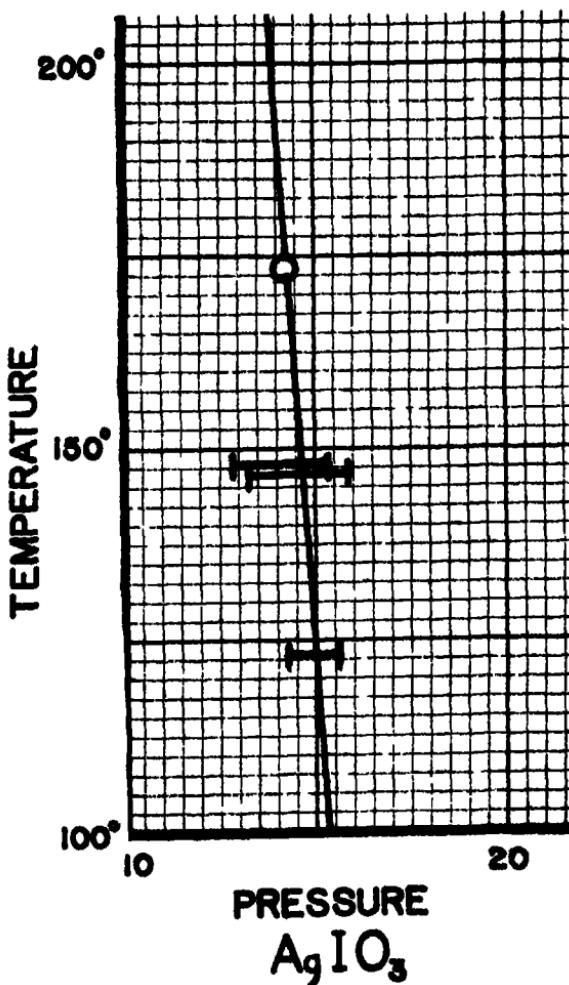


FIGURE 37 The transition line of  $\text{AgIO}_3$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

TABLE XIV  
TRANSITION PARAMETERS OF  $\text{RbClO}_4$

Pressure $\text{kg}/\text{cm}^2$	Temperature $^{\circ}\text{C}$	$\frac{dt}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	Latent Heat $\text{gm cal}/\mu\text{m}$
26,300	50	- 0238	00590	80 1	1 88
24,200	100	- 0238	00590	92 5	2 17
22,100	150	- 0238	00590	105 0	2 46
20,000	200	- 0238	00590	117 4	2 75

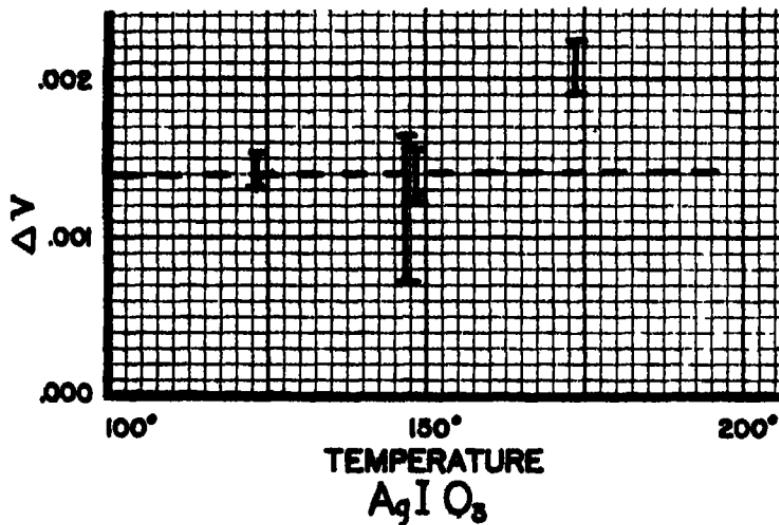


FIGURE 38 The volume change of the transition of  $\text{AgIO}_3$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

$\text{AgIO}_3$ . This was obtained from MacKay, made from "c p" chemicals by the action of  $\text{HIO}_3$  on  $\text{Ag}_2\text{CO}_3$ . The shearing curve was smooth, with no suggestion of any transition

With the volume apparatus a transition was found with small change of volume. At room temperature the transition is too sluggish to measure, measurements were made at four temperatures from  $123^{\circ}$  to  $174^{\circ}$ . The experimental results are shown in Figures 37 and 38, and the transition parameters in Table XV. The frictional creep with this substance was perhaps somewhat larger than usual, and this introduced some uncertainty into the transition measurements. It is perhaps not entirely ruled out, especially at the higher temperatures that there may be a second transition, close to the one shown.

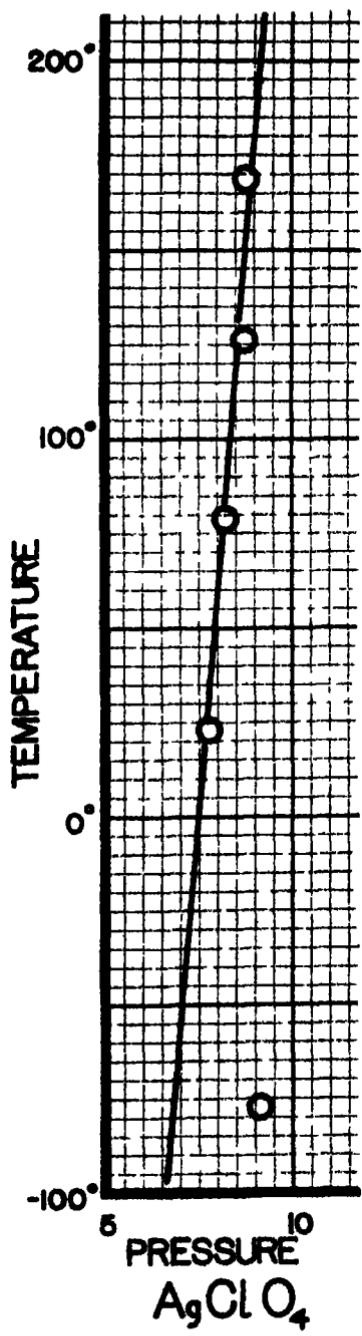


FIGURE 39 The transition line of  $\text{AgClO}_4$ , Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>

TABLE XV  
TRANSITION PARAMETERS OF  $\text{AgIO}_4$

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Heat gm cal/gm
15,300	100	-0.0714	.0014	7.3	17
14,600	150	-0.0714	.0014	8.3	19
13,900	200	-0.0714	.0014	9.3	22

$\text{AgClO}_4$ . This was obtained from MacKay, made from "c p" materials by the action of  $\text{Ag}_2\text{CO}_3$  on  $\text{HClO}_4$ . As supplied this probably contained free  $\text{HClO}_4$ , which was evaporated off at  $130^\circ$  in vacuum for three hours. The shearing curve was perfectly smooth and gave no evidence of a transition.

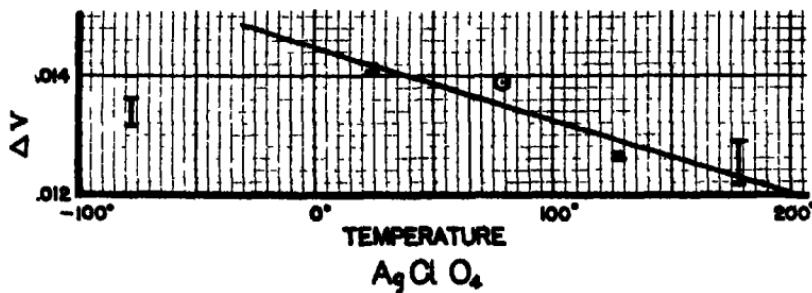


FIGURE 40 The volume change of the transition of  $\text{AgClO}_4$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature.

In the volume apparatus there is a transition with large change of volume, so that settings could be made on the two phase system. The transition runs very rapidly, and there was no appreciable region of indifference at any temperature from  $\text{CO}_2$  temperature to  $169^\circ$ . The experimental points are shown in Figures 39 and 40, and the transition parameters in Table XVI. The first measurements suggested another transition at  $\text{CO}_2$  temperature, but subsequent very careful measurements in the more sensitive apparatus showed nothing not attributable to friction, which sometimes may present puzzling aspects at this low temperature.

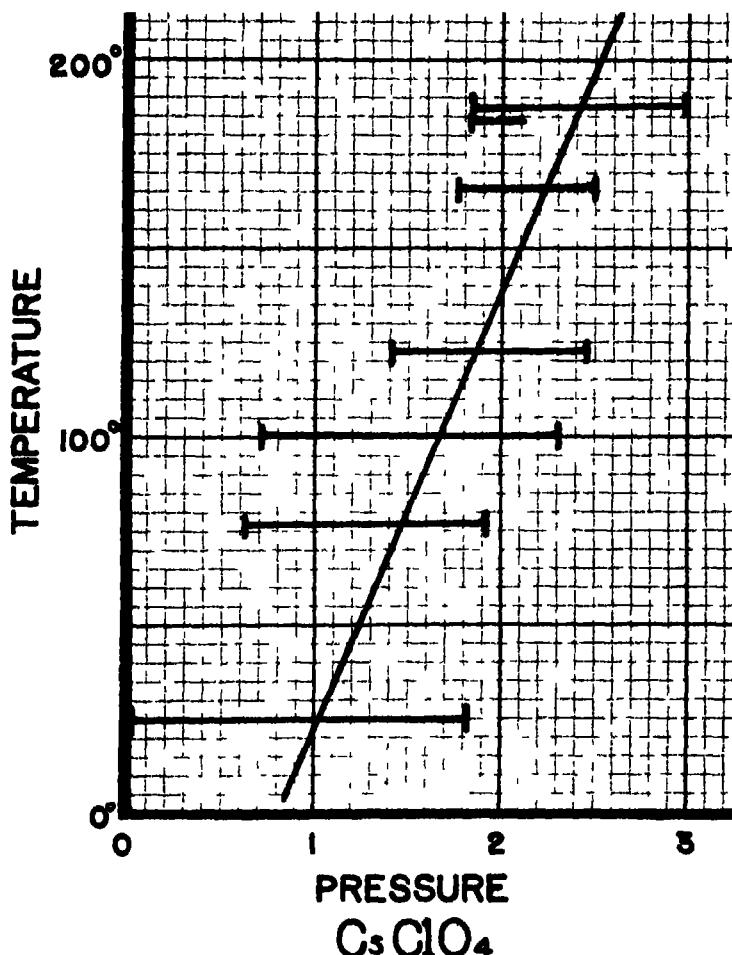


FIGURE 41 The transition line of  $\text{CsClO}_4$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

TABLE XVI  
TRANSITION PARAMETERS OF  $\text{AgClO}_4$

Pressure kg/cm <sup>2</sup>	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
7,500	0	+0.118	0.145	34.1	80
8,350	100	+0.118	0.132 <sub>5</sub>	41.9	98
9,200	200	+0.118	0.120	48.1	1.13

$\text{AgClO}_4$  is known to have a transition at atmospheric pressure at 155°. No trace of this was found at 169°, the pressure being too low.

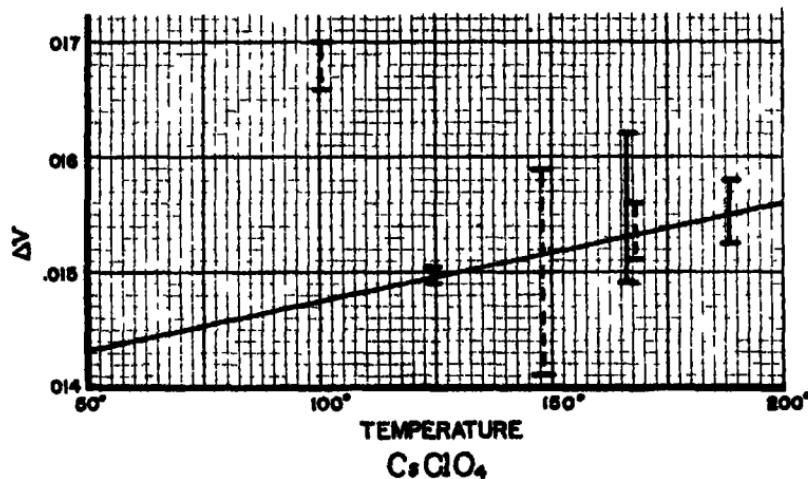


FIGURE 42 The volume change of the transition of  $\text{CsClO}_4$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

for this apparatus. In the case of this substance it is obviously possible to say with complete assurance that the high pressure form is different from that previously known at atmospheric pressure at high temperature. This fact lends plausibility to the assumption that the high pressure forms of the other perchlorates are also different from the known high temperature forms.

$\text{CsClO}_4$ . This material I owe to the kindness of Professor Baxter of the Harvard Chemical Laboratory. The shearing curve had a gentle upward curvature in the neighborhood of 20,000. Exploration with the volume apparatus disclosed a transition at very low pressures, so low that accurate measurements could not be made, it is doubtful

whether this transition corresponds to the inflection in the shearing curve. Measurements were made at four temperatures with the regular set-up, no other transitions were found to 50,000. In order to obtain greater accuracy special measurements were made with a special set-up using a piston of 0.375 instead of 0.25 inches diameter, and using about three and a half times as much material as usual. With this apparatus eight runs were made at temperatures between room temperature and 200°. The volume change is so large that equilibrium measurements could easily be made on the two phase system.

The experimental points are shown in Figures 41 and 42, and the transition parameters in Table XVII.

TABLE XVII  
TRANSITION PARAMETERS OF  $\text{CsClO}_4$

Pressure $\text{kg/cm}^2$	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	Heat $\text{gm cal/gm}$
800	0	0.114	0.1390	33.3	78
1,240	50	0.114	0.1432	41.8	98
1,675	100	0.114	0.1475	48.3	1.13
2,110	150	0.114	0.1517	56.3	1.32
2,550	200	0.114	0.1560	64.8	1.52

$\text{CsClO}_4$  is known to have a transition at atmospheric pressure at 219°, at which the ortho-rhombic low temperature modification changes to a cubic high temperature modification.

$\text{CsIO}_4$  This was obtained from MacKay, it was made from "c p" materials by the action of  $\text{HIO}_4$  on  $\text{CsHCO}_3$ . The shearing curve showed an inconspicuous upward inflection at 38,000 of doubtful significance.

The measurements with the volume apparatus were not as clean cut as could be desired, measurements were made at room temperature 147°, 169°, and 190°. At room temperature nothing definite was found. At the three higher temperatures there is without doubt a transition, but it is sluggish, and the volume change of the pure transition seems to be mixed up with something else, perhaps a slight decomposition. The transition runs at about 6,000 with increasing pressure, the reverse transition is not noticeable until pressure has been reduced back to atmospheric. The best mean of the transition pressures was 3000  $\text{kg/cm}^2$ , independent of temperature. The volume change is of the order of 0.0033  $\text{cm}^3/\text{gm}$ .

$\text{TlClO}_4$  This was obtained from MacKay, made from "c p" materials by the action of  $\text{Tl}_2\text{CO}_3$  on  $\text{HClO}_4$ . The shearing curve was

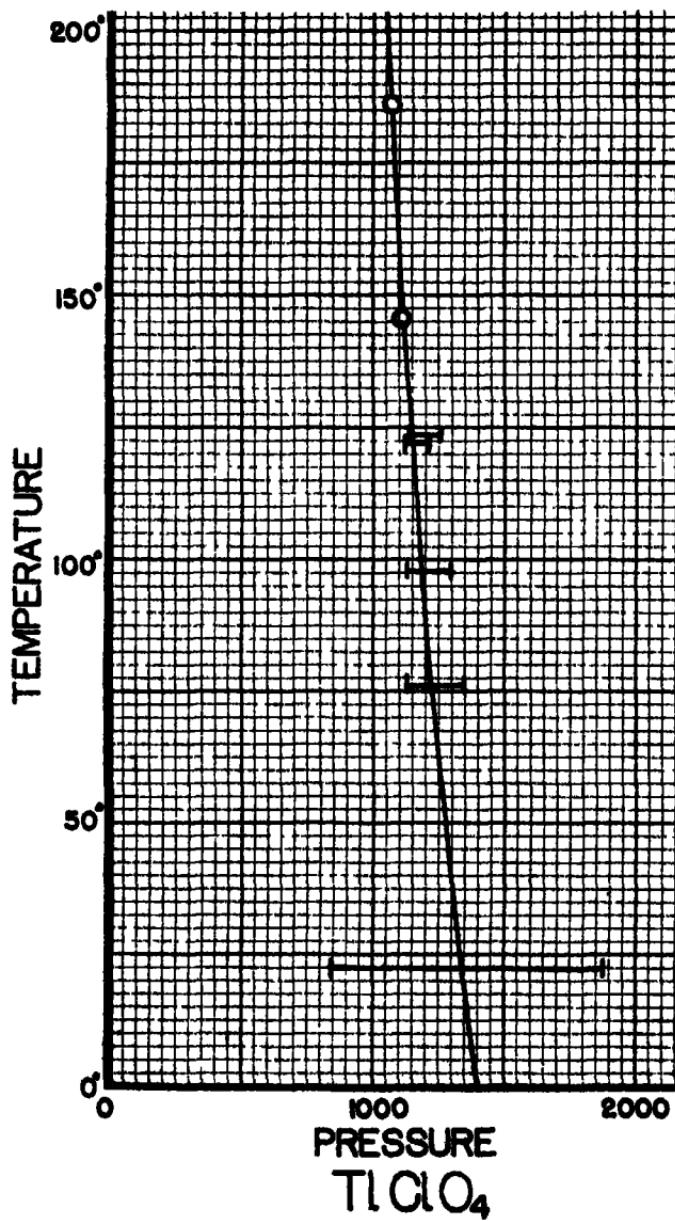


FIGURE 43 The transition line of  $\text{TiClO}_4$ , Centigrade temperature against pressure in  $\text{kg}/\text{cm}^2$

very unusual, having a maximum at 18,000, a minimum at 28,000, and beyond 28,000 rising convex toward the pressure axis. A transition is therefore to be expected.

Seven runs were made in the volume apparatus, with one filling, without accident, at various temperatures from room temperature to 180°. A transition was found with volume change sufficiently large to allow settings on the two phase system at the higher temperatures. At the lower temperatures the transition becomes very sluggish, and the band of indifference wide.

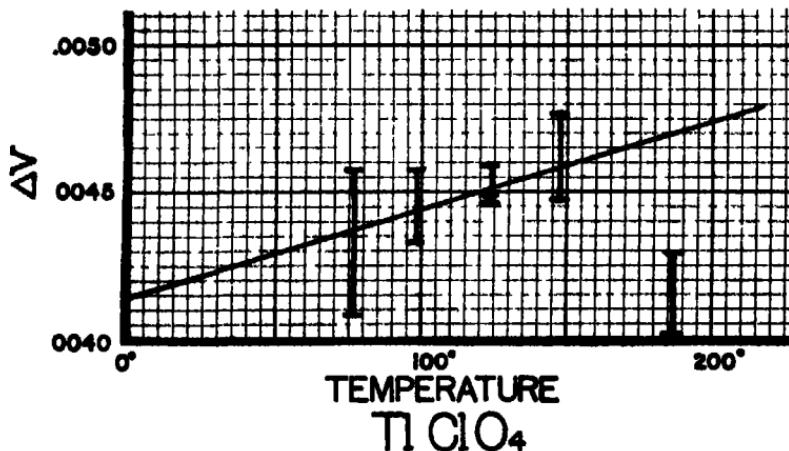


FIGURE 44 The volume change of the transition of  $\text{TiClO}_4$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

The experimental points are shown in Figures 43 and 44, and the transition parameters in Table XVIII. This substance is known to have a transition at atmospheric pressure at 266°. It is highly improbable that the transition line found here cuts the temperature axis at this temperature, so that it is probable that this high pressure phase is new.

TABLE XVIII  
TRANSITION PARAMETERS OF  $\text{TiClO}_4$

Pressure $\text{kg}/\text{cm}^2$	Temperature °C	$\frac{d\tau}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm}/\text{gm}$	Latent Heat $\text{gm cal}/\text{gm}$
14,000	0	- 0715	00414	15 8	370
12,800	50	- 0962	00429	14 4	337
11,900	100	- 1250	00444	13 2	311
11,200	150	- 1887	00459	12 2	287
10,600	200	- 2000	00474	11 2	263

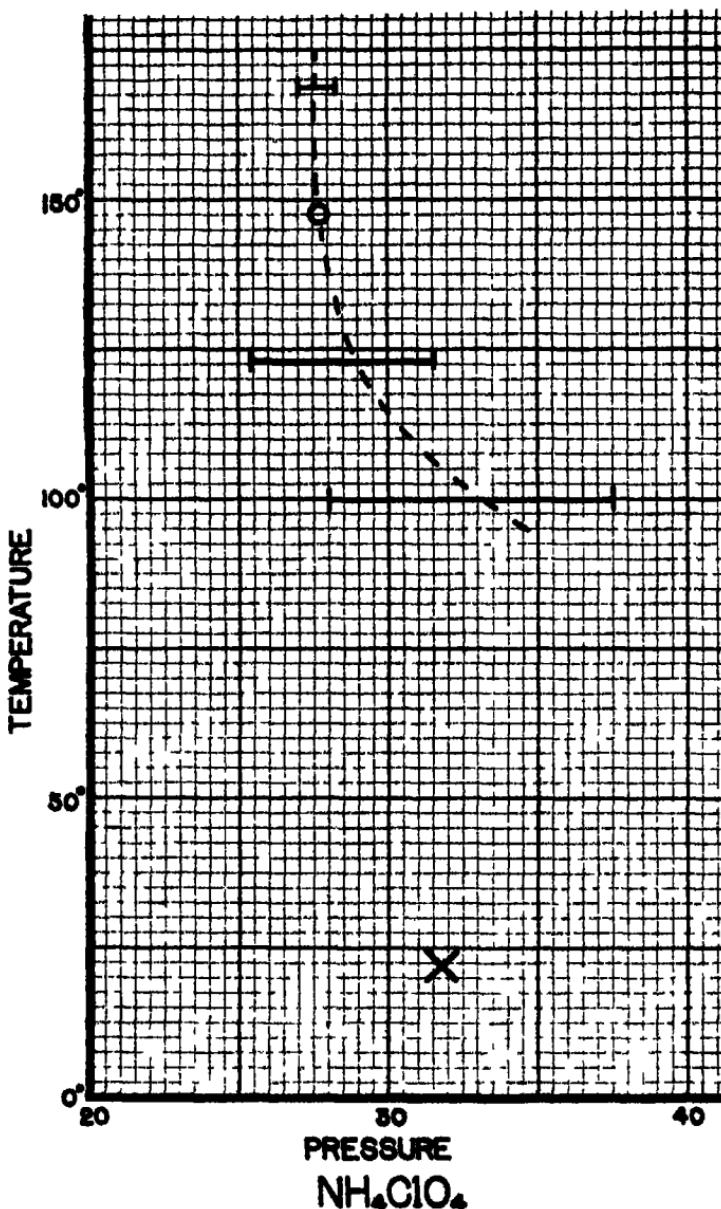


FIGURE 45 The transition line of  $\text{NH}_4\text{ClO}_4$ . Centigrade temperature against pressure in thousands of kg/cm<sup>2</sup>. The cross marks the point of discontinuity in the shearing curve

$\text{NH}_4\text{ClO}_4$  This was fresh "c p" stock from Eimer and Amend. The shearing curve had a maximum of cusp-like sharpness at 31,000. Four runs were made with the volume apparatus with a single filling without accident, from room temperature to  $108^\circ$ . The change of volume is too small to permit determinations of equilibrium with both phases present.

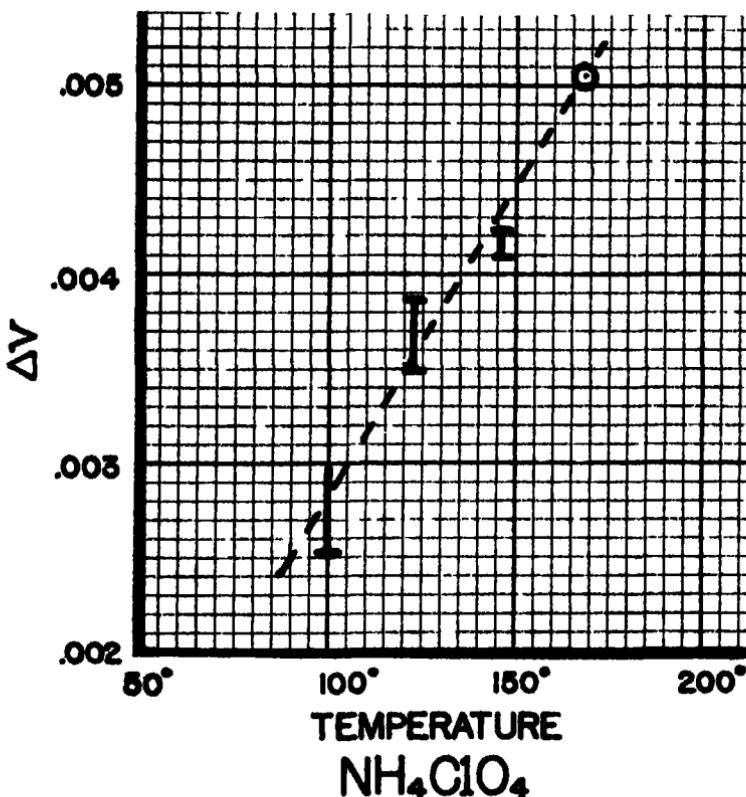


FIGURE 46 The volume change of transition of  $\text{NH}_4\text{ClO}_4$  in  $\text{cm}^3 \text{ gm}$  against Centigrade temperature

The experimental results are shown in Figures 45 and 46. The uncertainty in the transition curve due to the wide region of indifference is too great to permit computing a table of parameters, which can be obtained from the figures with all the accuracy warranted.

In spite of the insensitiveness of the measurements, however, this substance seems to be highly unusual.  $\Delta\tau$  falls off with decreasing temperature at a roughly linear rate and so rapidly that it should vanish at some temperature not far from  $0^\circ$ . The transition line is curved in a direction consistent with this. If the line continues with the same curvature it will have a horizontal tangent at the point at which  $\Delta\tau$  vanishes. This would be the only example of a transition curve with a minimum,  $HgI_2$  has a curve with a maximum. The evidence from the shearing curve is not favorable to this interpretation, which would demand an abnormally large displacement of equilibrium pressure with shear. It is perhaps not unreasonable to suppose that the maximum of the shearing curve is concerned with still another modification, and that the apparent progress of the transition line of Figure 45 toward a minimum will be arrested by a transition line and the appearance of a new phase.

$Na_2SO_4$ . This substance is known to be complexly polymorphic at atmospheric pressure, at least five modifications being recognized, one of which is metastable.<sup>12</sup> The transitions all occur above  $160^\circ$ . In general they are characterized by unusual sluggishness and capacity for superheating or subcooling. The shearing curve at room temperature showed no indication of a transition, the curve being entirely normal, concave toward the pressure axis, with rather well marked knee. Six runs were made in the volume apparatus, with a single filling, without mishap. The first run at room temperature yielded no obvious transition, the remaining five runs were spaced between  $100^\circ$  and  $175^\circ$ .

An ice type transition was picked up at  $147^\circ$  and  $100^\circ$ . This is very sluggish; at  $100^\circ$  it runs with appreciable velocity with increasing pressure at  $21,000 \text{ kg/cm}^2$ , and the reverse transition does not run with appreciable velocity until atmospheric pressure is reached. At  $147^\circ$  appreciable velocity with increasing pressure was not reached below  $14,500$ , where the transition ran to completion. On decrease of pressure it is probable that the transition did not run to completion at any pressure, restoration of the initial condition being brought about only by decrease of temperature. At  $100^\circ$  good values for the change of volume were found both with increasing and decreasing pressure. These two values were exactly the same, indicating that the two phases have sensibly the same compressibility. The identification of this transition with one of those studied by Kracek and Gibson is made possible by the change of volume, which corresponds to the transition IV-III (rather than the metastable change V-III).

The volume change decreases somewhat with increase of temperature, as it normally does with this type of transition

In addition to the known transition IV-III, another transition III-VI was found at high pressures, the new phase not being capable of existence at atmospheric pressure. This transition, like the other, is characterized by sluggishness and wide limits of indifference. Furthermore, the transition velocity is unsymmetrical on the two

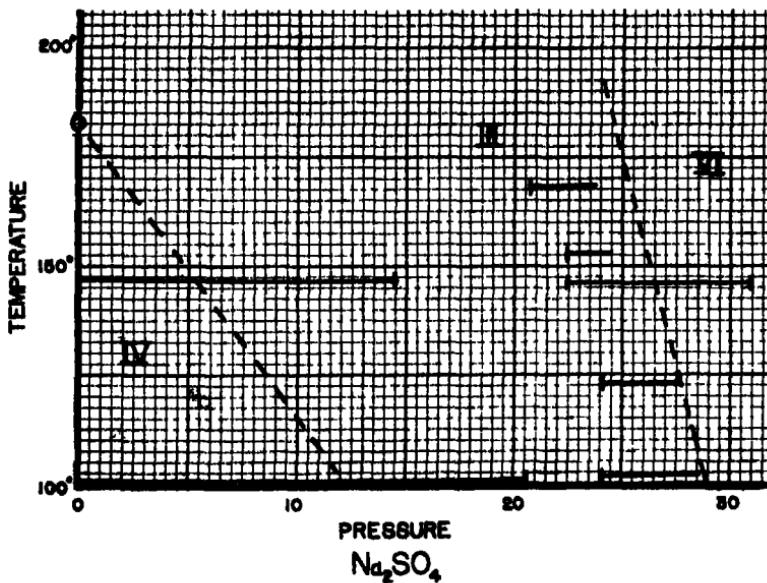


FIGURE 47 Part of the phase diagram of  $\text{Na}_2\text{SO}_4$ , part of the diagram at higher temperatures has been established by Kracek Centigrade temperature is plotted against pressure in thousands of  $\text{kg}/\text{cm}^2$

sides of the transition line. With increasing pressure the transition is spread through a considerable pressure range and runs so slowly that satisfactory evidence of its existence with increasing pressure was obtained only once, at 31,000  $\text{kg}/\text{cm}^2$ . However, after application of 50,000  $\text{kg}$  in 2,000 intervals on the regular two minute schedule the transition seems to be completed, and on release of pressure discloses itself much more definitely than with increasing pressure, satisfactory evidence of its existence having been found on five different occasions. The change of volume is smaller than for the

transition III-IV, being of the order of  $0.002 \text{ cm}^3/\text{gm}$ , this again decreases with increase of temperature.

The experimental values of transition pressure and temperature and of change of volume are shown in Figures 47 and 48. The values are not accurate enough to justify an attempt to compute the latent

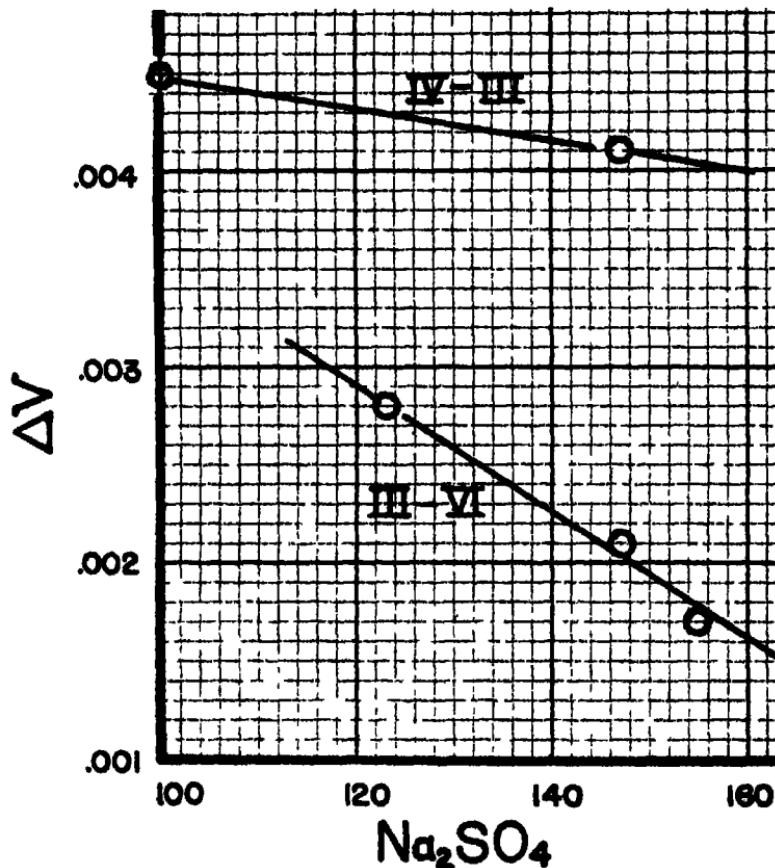


FIGURE 48 The volume change of two of the transitions of  $\text{Na}_2\text{SO}_4$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

heat. It is probable that the transition III-VI is also of the ice type, but rising much more steeply with temperature, and therefore with a smaller latent heat than III-IV. From Kracek and Gibson's latent

heat the slope of the transition line III-IV may be computed by Clapeyron's equation, this line is shown dotted in Figure 47. It is seen to be at least consistent with the very wide limits found above for the transition.

$KMnO_4$  The material was old laboratory stock. The shearing

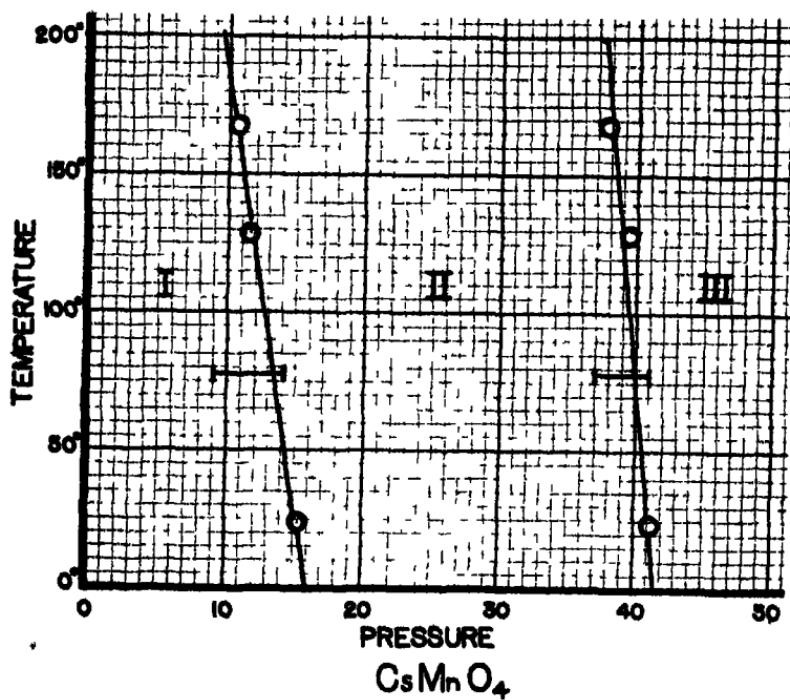


FIGURE 49 The phase diagram of  $CsMnO_4$ , Centigrade temperature against pressure in thousands of  $kg/cm^2$ .

curve showed a very pronounced upward break at 20,000  $kg/cm^2$ , strongly suggesting a transition. Four runs were successfully made with a single filling of the volume apparatus, twice at room temperature and twice at 100°. There is a transition, but the volume change is very small, and accurate results were not possible. The transition line runs nearly vertically, and therefore with little latent heat, at a pressure of 16,000  $kg/cm^2$ . The volume change is of the order of 0.0007  $cm^3/gm$ . The high pressure modification appears to be less compressible than the low pressure modification.

$CsMnO_4$ . This material had been prepared by Dr. O. Morrison of Williams College in 1932. It has been kept sealed and in the dark since then. I am indebted to Professor H. E. Bent of the Harvard Chemistry Department for telling me of the existence of this material and procuring it for me. The shearing curve was of the normal con-

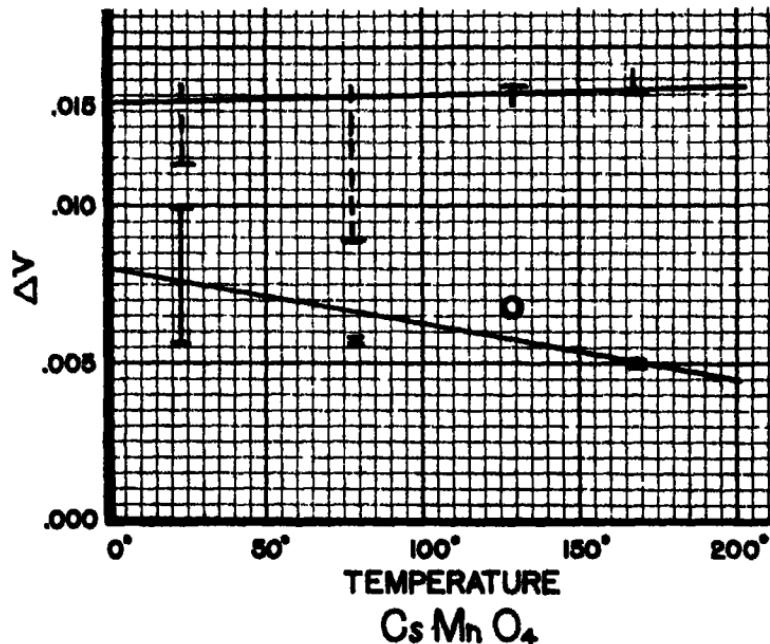


FIGURE 50 The change of volume of the transitions of  $CsMnO_4$  in  $\text{cm}^3/\text{gm}$  against Centigrade temperature

cave shape toward the pressure axis up to about 30,000  $\text{kg}/\text{cm}^2$ . At this pressure there was a definite break upward, suggesting a transition.

Measurements were made in the volume apparatus at five temperatures from  $\text{CO}_2$  temperature to  $168^\circ$ . There are two transitions, one at comparatively low and the other at high pressures. At  $\text{CO}_2$  temperature the transition was too sluggish to permit quantitative measurements, but there was enough creep during release of pressure to indicate that the high pressure transition had run during increase of pressure to a certain extent. The change of volume of both transitions is fairly large, and at the higher temperatures fairly definite equilibrium settings could be obtained. The change of volume of the

high pressure transition is made somewhat uncertain by the fact that the pressure is so high that during increase of pressure it was impossible to disentangle the transition from creep in the apparatus. The changes of volume of the same transition obtained with decrease of pressure suffer from uncertainty as to whether pressure had been held at the maximum long enough to permit the transition to run to completion. The changes of volume at the two highest temperatures, where the transition runs most rapidly, should have the least error from this source.

The experimental points are shown in Figures 49 and 50 and the transition parameters in Table XIX.

TABLE XIX  
TRANSITION PARAMETERS OF  $\text{CsMnO}_4$

Pressure $\text{kg/cm}^2$	Temperature $^\circ\text{C}$	$\frac{dt}{dp}$	$\Delta V$ $\text{cm}^3/\text{gm}$	Latent Heat $\text{kg cm/gm}$	Latent Heat $\text{gm cal/gm}$
I-II					
16,200	0	-0.0303	0.080	72.0	1.69
14,550	50	-0.0303	0.071	75.6	1.77
12,900	100	-0.0303	0.062	78.4	1.79
11,250	150	-0.0303	0.054	75.4	1.76
9,600	200	-0.0303	0.045	70.3	1.65
II-III					
41,800	0	-0.0477	0.133	76.0	1.78
40,550	50	-0.0477	0.134	90.7	2.13
39,500	100	-0.0477	0.135	105.6	2.47
38,450	150	-0.0477	0.136	120.6	2.83
37,400	200	-0.0477	0.137	135.4	3.18

$\text{Pb}(\text{C}_2\text{H}_5\text{O}_2)_2$ , anhydrous. The material was "tested purity" stock from Eimer and Amend, dehydrated by heating to  $130^\circ$  in vacuum. The shearing curve showed a sharp upward break at 26,000  $\text{kg/cm}^2$ , leading to the expectation of a transition.

The transition exploration with the volume apparatus was made with three different set-ups, one with the regular apparatus to a maximum pressure of 51,000, and two with the larger apparatus used when more sensitive measurements are required at lower pressures to a maximum of 23,000. The evidence seems unmistakable that there are three new modifications. The volume changes are small, however, and in some parts of the diagram the transitions are more than usually sluggish, so that it was not possible to get as satisfactory values for the parameters as usual.

The experimental points are shown in Figures 51 and 52, and the

transition parameters are collected in Table XX. It is obvious enough from the figures that there is considerable uncertainty with regard to the precise numerical results. The transition lines I-II

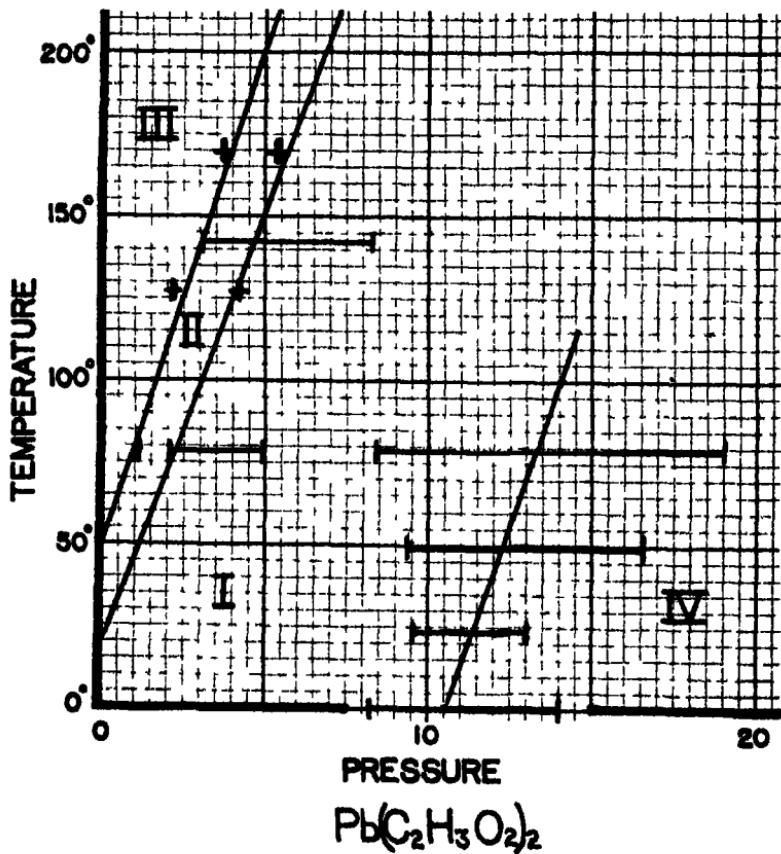


FIGURE 51 The phase diagram of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , Centigrade temperature against pressure in thousands of  $\text{kg}/\text{cm}^2$

and II-III have been drawn straight in the figure. This demands that there be transitions at atmospheric pressure not apparently noted in the literature. It is not at all ruled out that these transition lines are actually curved in such a way that they never cut the axis of atmospheric pressure. If this is the case, the modification called III

in the diagram is the modification normally encountered at atmospheric pressure. The precise location of the line I-IV is also in considerable doubt because of the unusual way in which the breadth of the region of indifference varies with pressure and temperature, although this is not without precedent. At 143° the transition was not detected out to 45,000 kg/cm<sup>2</sup>, doubtless because of too great sluggishness.

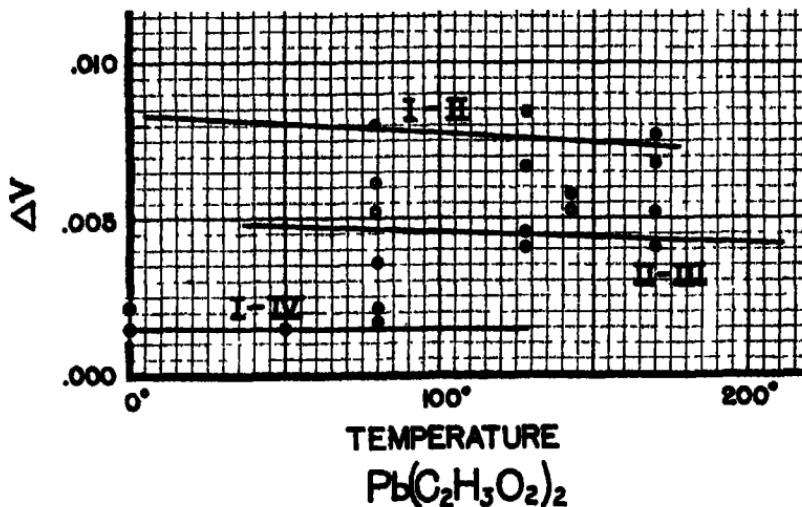


FIGURE 52 The volume change of the transitions of  $Pb(C_2H_5O_2)_2$  in  $cm^3/gm$  against Centigrade temperature

TABLE XX  
TRANSITION PARAMETERS OF  $Pb(C_2H_5O_2)_2$

Pressure $kg/cm^2$	Temperature $^{\circ}C$	$\frac{d\tau}{dp}$	$\Delta V$ $cm^3/gm$	Latent Heat $kg\ cm\ cm/gm$	Latent Heat $gm\ cal/gm$
I-II					
0	20	026	0082	92	2 2
5,000	150	026	0075	121	2 8
II-III					
0	50	030	0048	52	1 2
5,000	200	030	0043	68	1 6
I-IV					
10,500	0	0286	0015±	140	3 4
14,000	100	0286	0015±	200	4 6

## SUBSTANCES GIVING NEGATIVE RESULTS

In addition to the 35 substances just enumerated with transitions large enough to measure, a number of other substances were examined for new transitions with negative results. These substances were selected for one or another reason. In a number of instances there were breaks in the shearing curves which suggested a transition. Since the general character of the shearing curves of all these substances has been summarized in another paper on the general subject of shearing phenomena, it is not necessary to reproduce these shearing results here. The number of instances was comparatively small in which the shearing curves suggested transitions which were not found in the volume apparatus. In the majority of cases in which new forms were found not suggested by the shearing curves the existence of a new modification was suspected because of the chemical similarity of the substance to some other which was known to be polymorphic. The number of substances listed as polymorphic will depend importantly on the sensitiveness of the method in detecting small volume changes, for there seems to be no predilection for the volume changes of those transitions which have been measured to cluster around any special magnitude. Doubtless a more enthusiastic interpretation of small irregularities in some of the curves would have swelled the list of substances called polymorphic, but I have preferred to put the doubtful cases in almost every instance on the negative side. The general order of magnitude of a volume discontinuity which can be surely established is suggested by the smallest values already tabulated. Some substances are more favorable in this respect than others, the regularity of the volume measurements depending on the internal friction.

In the following, unless otherwise noted, the exploration which yielded negative results was made out to 50,000 kg/cm<sup>2</sup> at room temperature and at 150° C. The arrangement in the following is alphabetical, according to the metal in the salt.

*Ammonium* NH<sub>4</sub>IO<sub>3</sub> and NH<sub>4</sub>JO<sub>4</sub> definitely negative. NH<sub>4</sub>NO<sub>3</sub> gave irregularities at 150° between 10,000 and 20,000 which are probably due to the transitions already known, but the possibility of new transitions is not entirely ruled out.

*Antimony* SbBr<sub>3</sub>. This was tried because of its abnormally low melting point and unusual mechanical softness.

*Barium* BaS, tried only at room temperature to 39,000 kg/cm<sup>2</sup>.

*Bismuth* BiCl<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>. The two latter have shearing curves with very pronounced maxima, which must mean something drastic.

Since no polymorphic transition could be found in the volume apparatus, the interpretation of the shearing curve as indicating a decomposition to the metal is strengthened

*Cadmium* CdBr<sub>2</sub>

*Cesium* CsF, my expectation was strong that this would assume a body centered arrangement at high pressures like the other halogen compounds, but nothing was found at room temperature or 130° to 57,000. CsClO<sub>3</sub>, CsBrO<sub>3</sub>, CsIO<sub>3</sub>, all gave negative results. Three different set-ups were made with CsBrO<sub>3</sub>, this experiences some sort of an irreversible volume change at low pressures at 150°. X-ray analysis by Dr Jacobs showed no detectable alteration in the lattice. Perhaps a small amount of moisture may have been responsible.

*Chromium* Chrome alum, plus water of crystallization. Examined to 50,000 at room temperature, and at 75° to only 20,000, where the cylinder ruptured.

*Copper* CuS, Cu<sub>2</sub>S. The latter gave nothing at either temperature. The former gave nothing at room temperature, but at 150° appeared to have a transition between 2000 and 4000. However, the texts on chemistry emphasize the difficulty of getting the sulfides pure, and since no transition is recorded in the literature at atmospheric pressure, and NiS, which I had obtained from the same chemical supply house, was very definitely not chemically homogeneous, I did not pursue the matter further because of the probability of getting into unwelcome chemical complications.

*Lead* PbSe, the shearing curve has a very strong maximum, but the results with the volume apparatus were entirely negative, suggesting a decomposition under shearing stress. PbTe, gives also a maximum in shear, but is negative in the volume apparatus. Pb<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> was examined twice, there is an irreversible permanent change of volume at low pressures at 150°, for which no evidence could be found by Dr Hultgren on X-ray analysis. 2PbCO<sub>3</sub> Pb(OH)<sub>2</sub> Pb(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>)<sub>2</sub> 3H<sub>2</sub>O gave negative results, although the anhydrous salt has four modifications.

*Lithium* Li<sub>2</sub>SO<sub>4</sub> highly unusual shearing curve, surprising that no new modification was found.

*Manganese* Mn<sub>3</sub>O<sub>4</sub>

*Mercury* HgSO<sub>4</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, HgI Almost certain that these decompose to metallic mercury in shear.

*Nickel* NiS Irreversible changes at low pressures at 150° doubtless due to imperfect purity.

*Potassium* KBrO<sub>3</sub> Much time was spent on this compound, the appearance being that of a very sluggish transition spread over a wide

pressure range The evidence did not prove convincing, however, and I list it as negative  $KIO_3$ ,  $KClO_4$ ,  $KNO_3$

*Rubidium*  $RbClO_3$ ,  $RbBrO_3$ ,  $RbIO_3$ ,  $RbIO_4$

*Silver*  $Ag_2SO_4$ , the shearing curve is highly unusual, running horizontally from 15,000 to 33,000, then falling to a minimum at 45,000 and rising again Volume explorations were made at solid  $CO_2$  temperature, room temperature, and  $150^\circ$  There are indications of a transition line running nearly vertically in the neighborhood of 15,000, but I could not establish it certainly  $AgBrO_3$ ,  $AgIO_4$ , in addition to the run at room temperature, two runs were made at  $150^\circ$  and one at  $200^\circ$  At the two higher temperatures there is some sort of a volume change below 4000  $kg/cm^2$  which is at least partially reversible However, no simple interpretation of the results was evident, and I did not pursue the matter further  $AgClO_3$

*Sodium*  $NaF$ , the shearing curve definitely has a maximum near the end of the pressure range, leading to the expectation of a transition Because of the interest which any transition in this particularly simple compound would have, unusually careful exploration was made with the volume apparatus Two set-ups were used, with the second set-up runs were made at  $25^\circ$ ,  $125^\circ$ ,  $150^\circ$ , and  $175^\circ$  At first it appeared that there was a small break with decreasing pressure at pressures so high that the effect could not be certainly disentangled from creep in the apparatus, but more careful measurements showed nothing that was not certainly due to frictional irregularities at the highest pressures In any event it is certain that there is no transition with the large volume change associated with the change from face centered to body centered, which is the transition anticipated  $NaCl$ ,  $NaI$ , again the change from face centered to body centered was anticipated, particularly because of the behavior of the potassium and rubidium salts, but none was found The chances were probably best for finding it with  $NaI$   $NaIO_3$ ,  $NaCN$ ,  $NaNO_3$ ,  $NaSCN$  Particularly careful search was made with the latter, since irregularities on the first set-up indicated a possibility at low pressures Repetition with the more sensitive apparatus at  $175^\circ$  gave nothing

*Strontium*  $SrO$ ,  $SrBr_2$ ,  $SrS$ ,  $SrSO_4$

*Thallium*  $TlClO_3$ , explodes at  $150^\circ$  at atmospheric pressure, repetition at  $125^\circ$  gave nothing  $TlBrO_3$ , explodes at atmospheric pressure at  $140^\circ$ , repetition at  $125^\circ$  gave nothing  $TlIO_3$ , negative at room temperature and  $125^\circ$   $TlIO_4$ , the first set-up at four temperatures up to  $168^\circ$  displayed an unexplained creep at low pressures Repetition at four temperatures up to  $125^\circ$  yielded nothing positive  $Tl_2SO_4$ ,  $TlNO_3$

Zinc ZnO, ZnS, ZnSO<sub>4</sub>, 2ZnCO<sub>3</sub>·3Zn(OH)<sub>2</sub>  
Zirconium ZrO<sub>2</sub>

### DISCUSSION

The most obvious question for consideration is whether the extension of pressure range from 12,000 kg/cm<sup>2</sup>, the range of my former investigation of polymorphism, to 50,000 discloses any important change in the general character of the phenomena. A graphical summary of my earlier work will be found, for example, on pages 232 and 233 of *The Physics of High Pressure*. Here are collected the phase diagrams of 36 substances, each diagram in itself being approximately square, the pressure range up to 12,000, as abscissa, occupying the same length as the temperature range, 200°, as ordinate. The rough impressionistic aspect of all these diagrams is of transition lines sweeping over the complete range of both pressure and temperature at approximately 45°. That is, as a very rough average, 12,000 kg/cm<sup>2</sup> produces a change of transition temperature of the order of 200°. Departures from this rule, of which there are many, are mostly in the direction toward verticality in the lines, that is, a 200° change of temperature for less than 12,000 kg/cm<sup>2</sup>. If now, one plots the new data of this paper in similar square diagrams, the range of abscissas now being 50,000 instead of 12,000 kg/cm<sup>2</sup>, and the temperature range being 200° as before, the impressionistic aspect changes. The transition lines now run approximately vertically across the diagrams. By far the larger number of transition lines sweep completely across the diagram for a pressure change of 10,000 kg/cm<sup>2</sup> or less. There is no apparent systematic difference in the slope of lines at the low pressure and the high pressure ends of the diagram. The different impressions given by the two sets of diagrams appears to be the result merely of the change in the scale of abscissas, and there is no significant alteration in the relative effects of temperature and pressure at high pressure. The same thing may be shown by plotting the mean slope of the various transitions lines against the mean pressure, there is no significant bunching of points in any part of the diagram.

Such a diagram does bring out, however, one significant difference between the present and the former results, namely the relative number of lines with positive and negative slopes. A negative slope,  $\frac{d\tau}{dp}$ , in itself means a state of affairs that one might be inclined to class as abnormal, for such a line means that the phase stable at higher temperature has the smaller volume. Such a state of affairs is definitely

abnormal if the two phases are liquid and solid. Only three examples of falling melting lines have been examined, water, bismuth, and gallium, in each of these cases the line falls over only a limited pressure range. Beyond that range the modification of the solid stable at low pressures is replaced by a new high pressure form, with smaller volume than the liquid, and the melting curve rises as is normal. One might perhaps anticipate the same situation for solid-solid transitions. Previous work to 12,000 had disclosed an unexpectedly large number of falling transition lines. Out of 59 examples, 14, or 24% had negative slopes. Analogy with the melting curves would lead to the expectation that at higher pressures falling transition lines would give place to rising lines, or that the total percentage of falling lines would be less for a pressure range of 50,000 than for 12,000. The opposite turns out to be the case, however. In the new work there are 44 transition lines the slope of which can be established with sufficient accuracy, and of these 19, or 43%, have negative slopes. That is, as the pressure range increases the number of "abnormal" cases increases instead of decreasing. There seems to be no inherent instability in an "abnormal" relation between the volumes of *solid* phases. An abnormal volume relation means that when the transition runs from the low pressure to the high pressure phase the system absorbs energy from the surroundings both in the form of heat and of mechanical work.

A transition line must plunge into the pressure axis vertically at the absolute zero of temperature if the third law is valid. This, combined with the fact that most of the transition lines are nearly vertical in the temperature range covered above, must mean that most of the transition lines investigated above will cut the pressure axis at absolute zero. That is, pressure polymorphism at absolute zero is a comparatively common phenomenon, and there is no tendency for it to become less common as the pressure range is increased.

We next examine statistically the volume differences between the phases. For this purpose the volume changes given above in the tables should be converted into percentage changes by multiplying by the densities. We may study in the first place the relative frequency of the different magnitudes of  $\Delta v$  by plotting the number of examples against the logarithm of the percentage volume change. In this way a distribution curve will be found of practically constant amplitude from volume changes of 11% down to 0.8%. Below this the distribution amplitude tails off, eventually disappearing at the smallest volume change measured above, 0.04%. The interpretation

of the tailing off is without doubt that the sensitiveness of the method is not sufficient to detect the small volume changes. Since the logarithmic scale reaches indefinitely down toward small numbers the significance of this result would seem to be that one may expect polymorphism to be a more and more frequent phenomenon the more one increases the sensitiveness of the method for detecting volume changes. This constitutes the quantitative justification for a remark made earlier in this paper.

The distribution of the changes of volume may also be studied as a function of the mean pressure of the transition. Again it will be found that there is no significant bunching of points in any part of the diagram, that is, there is no tendency for the volume changes to become either smaller or larger on the average as the mean pressure of the transition increases.

A statistical study may be made of the number of phases which exist for the different substances. If the substances formerly studied are included, the following result is obtained:

Number of phases	2	3	4	5	6	7
Number of examples	45	13	7	0	3	1

Very roughly, the number of examples falls off geometrically as the number of phases increases arithmetically. That is, the chance that a substance will exhibit a new phase is not affected by the fact that it may already have exhibited polymorphism.

All of these considerations display polymorphism as an essentially haphazard phenomenon. Polymorphism is likely to hit a substance at any time, irrespective of whether it has already shown it or not and irrespective of the pressure, and the accompanying volume change will be selected at random in the range from zero up to something probably not much more than 10 per cent. If the volume range from which haphazard selection is made is properly expressed on a logarithmic basis, as would be suggested by our frequency analysis, this means an unlimited amount of polymorphism in the domain of small volume changes. Such is not inconsistent with other pictures. The forces which hold solids together are known to be of various kinds, such as the ionic forces in salts, van der Waals' forces in solid inert gases, exchange and electronic forces in metals, and various combinations of these. Polymorphic transitions may be recognized corresponding to one or the other of these or to changes from predominantly one to predominantly another. There would seem to be no hard and fast line of demarcation between transitions produced by a change in the predominant type of force and the finer changes due to rearrangements.

of energy levels of any sort. For this reason one may expect to find polymorphism increasingly prevalent as one increases the sensitivity of measurement. Eventually the phenomena will doubtless receive adequate theoretical explanation, but at present the complexities are so great that a statistical study such as we have made here can disclose only a haphazard situation.

We next examine the energy changes in the transitions. It is a consequence of the fact that neither the slope nor the changes of volume exhibit any systematic trend with increasing pressure that the latent heat exhibits no trend either. The difference of energy, however, does exhibit a trend. For this can be written as  $\Delta E = L - p\Delta v$ , and since neither  $L$  nor  $\Delta v$  exhibits a trend, the trend of  $\Delta E$  is the same as the trend of  $p$  itself. That is, at the higher pressures more and more substances increase in internal energy on passing from the low pressure to the high pressure modification, and this increase of energy becomes on the average more and more nearly equal to the work done by the external pressure acting through the change of volume. At the absolute zero of temperature the relations are especially simple. Here there are no heating effects, and the whole system can be described in mechanical terms. The internal pressure in each phase is equal to the external pressure, the increase of internal energy is  $p\Delta v$ , and the mean internal pressure during the transition (defining the mean internal pressure as that quantity which multiplied by the change of volume gives the change of energy) is exactly the same as the internal pressure in the initial and the final phases. This increase of internal energy points to a rearrangement in the structure of atoms and molecules. For Schottky's theorem, written for 0° Abs., gives

$$\Delta E_{kin} = 4p\Delta v$$

Since  $\Delta v$  must be negative on passing from the low to the high pressure modification, this means that the total internal kinetic energy is less by the amount  $4p|\Delta v|$  in the high pressure modification. The total internal kinetic energy comprises the contribution arising from mass motion of the atoms, and the part from the internal motions of its electrons. In general, the high pressure phase will be a phase with greater stiffness of constraints, and therefore a greater natural frequency. The kinetic energy of mass motion arising from the zero point energy  $\frac{1}{2}hy$  will therefore in general be greater in the high pressure phase. This demands that the internal kinetic energy of electronic motion decrease by an amount numerically greater than

$4p\Delta v$  Under normal conditions this would mean an increase in size of the atoms, a result so paradoxical that one seems forced to conclude that the electrons which contribute to the change of kinetic energy cannot be associated with particular atoms

At temperatures above 0° Abs there seems no reason to suppose that the decrease of internal non-classical kinetic energy does not continue to be greater than  $4p\Delta v$ . This is materially larger than the energies in the form of latent heat concerned with the transitions. For example, in the above tables the largest latent heat is that of the II-IV transition of KCN at 20° and 20,000 kg/cm<sup>2</sup>. At this transition point the term  $4p\Delta v$  is nearly 12 times as great as the latent heat. That is, in the temperature range of this work and at pressures above 20,000 ordinary thermal phenomena are a comparatively minor effect superposed on the quantum phenomena which would be exhibited in their purity at 0° Abs.

Although not large compared with ionization energies, the energy  $4p\Delta v$  is nevertheless quite appreciable when expressed in electronic terms. In a previous paper<sup>12</sup> I have calculated that at the II-III transition of bismuth at 25,000 kg/cm<sup>2</sup> the term  $4p\Delta v$  amounts to 0.18 electron volts per atom.

The change of internal energy during a transition may be written

$$\Delta E = \Delta v \left[ \frac{L}{\Delta v} - p \right] = \Delta v \left[ \tau \frac{dp}{d\tau} - p \right]$$

The factor  $\tau \frac{dp}{d\tau} - p$  may be regarded as a sort of average "internal" pressure during the transition, and the term  $\tau \frac{dp}{d\tau}$  as an average "thermal" pressure analogous to the familiar "thermal" pressure  $\tau \left( \frac{\partial p}{\partial \tau} \right)_v$  of homogeneous phases. I believe, however, that this analysis into "internal" and "thermal" pressures can be regarded as only a formal matter, without especial significance with regard to the mechanism. For we have already seen that in 40 per cent of the cases  $\frac{dp}{d\tau}$

is negative, which would demand a *negative* thermal pressure during the transition. This is a difficult sort of thing to visualize, particularly when the "thermal" pressures of the phases separately are doubtless positive. In fact, I very much question whether the conventional analysis into "internal" and "thermal" pressures remains profitable even for homogeneous phases at high pressures where the

internal sources of kinetic energy which may be drawn on become more important than the classical thermal sources

In the cases above which could be measured with sufficient accuracy the energy increases on passing from the low to the high pressure modification in 78 per cent of the cases. That is, the thermal effect overbalances the mechanical work in only 22 per cent of the cases. This is in sharp contrast with the behavior on melting, in all the cases of melting studied up to  $12,000 \text{ kg/cm}^2$  the thermal term overbalances the mechanical work, usually by a factor of several fold.

It remains now to comment on various specific features. By far the most extensive group of chemically related substances examined above comprises the chlorates, bromates, iodates, perchlorates and periodates of the univalent radicals Na, K, Rb, Cs, Ag, Tl, and  $\text{NH}_4$  (the chlorate and bromate of  $\text{NH}_4$  were omitted because of danger of explosion in ordinary handling at atmospheric pressure). My attention was attracted to this family because the seven perchlorates are known to be polymorphic at atmospheric pressure,<sup>14</sup> changing over from a rhombic to a cubic modification at temperatures which range from  $155^\circ$  to  $308^\circ$ . All seven cubic modifications seem to be similar in lattice structure, but the rhombic modifications of Na and Ag are different in type from the five other rhombic modifications. One or two of the easily obtained perchlorates proved to be polymorphic under pressure, and this suggested a study of the entire family. Most of the compounds were specially made by MacKay. Six of the seven perchlorates proved to be polymorphic under pressure, the potassium compound giving the only negative result. There is no apparent connection between the new high pressure modifications and the transition at atmospheric pressure, as inspection of the phase diagrams shows at once. It would be natural to expect some resemblance between the new high pressure forms. The magnitude of the volume change would seem to be the best clue to this. The caesium and silver salts show volume changes of 5.0 and 6.0 per cent respectively, so that at first it would be natural to correlate their two high pressure forms. This is highly questionable, however, when one reflects that the low pressure rhombic form of the silver compound is known to be different from that of the caesium compound. The other volume changes are distributed as follows: Na salt, 0.4% and 3.5%, Rb, 1.7%,  $\text{NH}_4$ , 0.8% and Tl, 2.2%. It is perhaps not improbable that the high pressure forms of Rb,  $\text{NH}_4$ , and Tl are analogous, but there seems no reason to think that the other high pressure forms in this group are related. This was a surprise to me in view of the close similarity of

the phenomena at atmospheric pressure. The wide prevalence of pressure polymorphism in this group must appear to be more or less of a coincidence.

Contrasted with six out of seven cases of pressure polymorphism among the perchlorates are at most eight out of the remaining twenty-four in all the other compounds of the family. This proportion is about what it is for compounds selected at random. The exuberant polymorphism exhibited by  $\text{NaClO}_3$ , the first compound tried, proved a false clue to the rest of the family.

Another family in which polymorphism is of frequent occurrence is the nitrates of the univalent radicals. Exploration of the phase diagrams of six of these up to 12,000 kg/cm<sup>2</sup> was made some time ago.<sup>10</sup> Three of these, Ag, Cs, and Rb are now found to yield new forms in the extended pressure range. Of these, it is not improbable that the high pressure forms of  $\text{CsNO}_3$  and  $\text{RbNO}_3$  are analogous, since the atmospheric forms from which the high pressure form springs is rhombic in each case, and the change of volume at the transition is small. Except for this, there does not seem to be any particular resemblance between the phase diagrams of the various nitrates. In particular, extension of the pressure range has not proved to result in supplementing previously known phase diagrams in such a way that resemblances are disclosed which were formerly concealed by too low a range of pressure. The frequent occurrence of polymorphism in the nitrates appears to be a somewhat unsystematic phenomenon, for which the clue is not yet apparent.

This sort of discussion could be considerably extended, but always to the same conclusion, namely that the phase diagrams do not exhibit the similarities which might be anticipated because of chemical similarity. The one outstanding exception is the transition from the face centered to the body centered arrangement in the halides of  $\text{NH}_4$ , Rb, and K. But even in the simple NaCl type of structure other sorts of change are possible, as shown by the obscure low pressure change of  $\text{RbCl}$ , the small transitions of  $\text{AgCl}$  and  $\text{AgBr}$ , and the complicated phase diagram of  $\text{KCN}$ , with its large volume changes. The comparative unimportance of the chemical factor in determining polymorphic change is consistent with the suggestion presented earlier in the discussion, namely that during a polymorphic change we are concerned with internal rearrangements more deep seated than those involved in the molecular phenomena of chemistry.

I am much indebted to my assistant, Mr L H Abbot, for making most of the readings, and to the Rumford Fund of the American

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REFERENCES

- <sup>1</sup> P W Bridgman, Phys Rev **48**, 893-906, 1935
- <sup>2</sup> P W Bridgman, *Ibid* **48**, 825-847, 1935
- <sup>3</sup> P W Bridgman, Proc Amer Acad **61**, 57-90, 1926
- <sup>4</sup> P W Bridgman, *Ibid* **70**, 71-101, 1935
- <sup>5</sup> P W Bridgman, *Ibid* **46**, 325-341, 1911
- <sup>6</sup> P W Bridgman, *Ibid* **71**, 387-460, 1937
- <sup>7</sup> P W Bridgman, *Ibid* **67**, 365, 1932
- <sup>8</sup> P W Bridgman, *Ibid* **51**, 104, 1915
- <sup>9</sup> P W Bridgman, *Ibid* **51**, 81, 1915
- <sup>10</sup> P W Bridgman, *Ibid* **51**, 590, 1916
- <sup>11</sup> P W Bridgman, *Ibid* **51**, 78, 1915
- <sup>12</sup> F C Kracek and R E Gibson, Jour Phys Chem **34**, 188-206, 1930
- <sup>13</sup> P W Bridgman, Rev Mod Phys **7**, 17, 1935
- <sup>14</sup> H Braekken und L Harang, ZS f Krist **75**, 538-549, 1930

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Massachusetts Institute of Technology, No 384 )

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TEMPERATURE SCALE V**

**THE REPRODUCIBILITY OF THE ICE POINT AND THE TRIPLE-  
POINT OF WATER THE TEMPERATURE OF THE  
TRIPLE-POINT OF WATER**

**BY JAMES A. BEATTIE, TZU-CHING HUANG,  
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#### 1 INTRODUCTION

THE ice point,  $0^{\circ}$  C., is one of the fixed points on the absolute temperature scale and on the International Temperature Scale. It is defined as "the temperature at which pure, finely divided ice is in equilibrium with pure, air-saturated water under standard atmospheric pressure"<sup>1</sup>. The reproducibility of the ice point has been questioned in recent years and the advisability of using the triple-point of water (the temperature at which pure ice, liquid water, and water vapor are in equilibrium) considered. The temperature of the ice point is lower than that of the triple-point of water by  $0.00980^{\circ}$  C., of which  $0.00743^{\circ}$  C. is due to the effect of pressure on the freezing point of pure water and the balance due to the freezing point depression resulting from the solution in water of the gases composing the atmosphere.

Moser<sup>2</sup> states that the ice point prepared according to the method given by Henning<sup>3</sup> is reproducible to  $0.002$  to  $0.003^{\circ}$  C., he found that the temperature of the triple-point of water could be reproduced to  $\pm 0.5 \times 10^{-4}^{\circ}$  C., and remained constant within this variation for

<sup>1</sup> See G. K. Burgess, Bur. Standards J. Research, 1, 635 (1928).

<sup>2</sup> H. Moser, Ann der Physik, (5) 1, 341 (1929).

<sup>3</sup> F. Henning, "Temperaturmessung," p. 231, Vieweg (1915).

some days. He found that the temperature of equilibrium between ice and pure water is lowered  $0.00748 \pm 0.00005^\circ\text{C}$  by an increase in pressure of 760 mm. This corresponds to a lowering of  $0.00743^\circ\text{C}$ , when the pressure is increased from 46 mm of mercury (the triple-point vapor pressure) to 760 mm. He computed the effect of air saturating the water to be a further lowering of  $0.0024^\circ\text{C}$ , giving a total of  $0.0098^\circ\text{C}$  for the difference between the ice point and the triple-point of water.

White<sup>4</sup> considered that the variations encountered in the ice point were due to impurities on the surface of the ice. He made 17 "cold cells"—closed vessels containing an ice-water mixture immersed in an ice bath—each with two outlets, one for introducing fresh water and the other for removal of the water in the cell. He found that when first prepared the temperatures of 14 of the cold cells differed by  $0.001^\circ\text{C}$  or more, when, however, the water in the cold cells was replaced by fresh, air-saturated water cooled to  $0^\circ\text{C}$ , the temperatures of all of the cells could be brought to within  $0.5$  to  $1.0 \times 10^{-4}^\circ\text{C}$  of each other.

Thomas<sup>5</sup> was able to reproduce the ice point within  $1.0$  to  $1.5 \times 10^{-4}^\circ\text{C}$  over a period of months. He measured the difference between the ice point and the triple-point of water and obtained a value of  $0.0097^\circ\text{C}$  at an average barometer reading of 750 mm.

## 2 VARIABLES AFFECTING THE TEMPERATURE OF THE ICE POINT

*Pressure.* At a distance  $h$  mm below the level of the water, the temperature  $t^\circ\text{C}$  of equilibrium between ice and water saturated with air at  $0^\circ\text{C}$  and at a barometric pressure of  $p$  mm of mercury is

$$t = -0.00980 \frac{p - 760}{760} - \frac{0.00748 \times 0.999868}{760 \times 13.5955} h \\ = -1.29 \times 10^{-4} (p - 760) - 0.072 \times 10^{-4} h \quad (1)$$

The barometric correction is not negligible. In a place such as Denver, Colorado where the average atmospheric pressure is 630 mm, the barometric correction amounts to  $17 \times 10^{-4}^\circ\text{C}$ . The maximum variation in atmospheric pressure at Cambridge, Massachusetts amounts to about 40 mm, which corresponds to a variation of  $5 \times 10^{-4}^\circ\text{C}$  in the temperature in an ice point cell.

A depth of immersion of a thermometer in an ice point cell of 15 cm necessitates a correction of  $-1 \times 10^{-4}^\circ\text{C}$ .

<sup>4</sup> W. P. White, J. Am. Chem. Soc., 56, 20 (1934).

<sup>5</sup> J. L. Thomas, Bur. Standards J. Research, 12, 323 (1934).

*Purity of Ice and Water* The specific conductances of water obtained from several sources are given in Table I. All conductances were determined at 10° C,<sup>6</sup> and it was assumed that no CO<sub>2</sub> was lost or gained by the water during the short time required to make the measurement. The corresponding freezing point depression — Δt was computed from the equation

$$-\Delta t = 2 \times 1858 \times 1000 (L - L') / \Lambda_0 \quad (2)$$

where 1858 is the limiting molal freezing-point depression of water, L and L' are, respectively, the specific conductance of the sample of water and that of pure water saturated with air at 0° C and 760 mm total pressure, and Λ<sub>0</sub> is the limiting equivalent conductance of the impurity. We assumed that the impurity was sodium chloride for which Λ<sub>0</sub> has the value 67 ohms<sup>-1</sup> at 0° C and 89 at 10° C. The specific conductance of water saturated with air at 0° C and 760 mm is  $0.7 \times 10^{-4}$  when measured at 0° C and  $0.9 \times 10^{-4}$  when measured at 10° C (See Table II). Thus

$$-\Delta t = 55(L - 0.7 \times 10^{-4}) \quad (\text{when } L \text{ is measured at } 0^\circ \text{ C}) \quad (3)$$

$$-\Delta t = 42(L - 0.9 \times 10^{-4}) \quad (\text{when } L \text{ is measured at } 10^\circ \text{ C}) \quad (4)$$

The data given in Table I show clearly that the impurities in the different kinds of water and ice,<sup>7</sup> the raw materials of an ice point cell, account for a variation in temperature of only  $0.4 \times 10^{-4}$  °C. The introduction of the impurities must take place in the preparation of the cell, as suggested by White;<sup>4</sup> and this is shown by the data on the ice point cells A and B. In the preparation of both cells ordinary precautions to prevent the introduction of impurities were taken. Clear ice cut into pieces about 12 cm on a side, were rinsed with distilled water, and shaved into a fine snow by means of a commercial motor-driven shaver. The ice point cell (a silvered Dewar tube), the stainless-steel stirring rod and the case of the thermometer were rinsed with distilled water and allowed to drain. For cell A the shaved ice was transferred to the Dewar tube by the bare hands which had been rinsed with distilled water, for cell B the ice was transferred by

\* We wish to thank Professor George Scatchard and Miss Marjorie Allen (now Mrs Manson Benedict) for making the conductance measurements. The method was that of G. Scatchard, P. T. Jones, and S. S. Prentiss, J. Am. Chem. Soc., 54, 2676 (1932).

<sup>7</sup> For the determination of the specific conductances of water obtained from melted ice, a single piece of the ice was washed, melted and the specific conductance measured without any attempt to air-saturate the water. This operation corresponds to what takes place in an ice point cell.

means of a glass vessel. The water, which was added to the cell in sufficient quantity to make a mush that was easily stirred, had been stored for 12 hours in an unstoppered pyrex bottle in an ice-chest, whereby its temperature fell to  $5^{\circ}\text{ C}$ , and immediately before use had been cooled to  $0^{\circ}\text{ C}$  by the addition of pieces of washed ice about 2 cm on a side, and air-saturated by frequent vigorous shaking for a period of one-half hour. After the thermometer had been inserted, the ice-water mixture was stirred by raising and lowering the stirring-rod which had a loop in a horizontal plane, and the ice pressed down until a few millimeters of water showed above the surface of the ice. In the preparation of cell A the ice was transferred to the ice point cell by the bare hands which had been rinsed with distilled water, sufficient impurity was thereby introduced to lower the temperature by a computed amount of  $6$  to  $10 \times 10^{-4}^{\circ}\text{ C}$ . In the preparation of cell B the ice was transferred by means of a glass vessel, the computed freezing point lowering due to impurity was  $1$  to  $2 \times 10^{-4}^{\circ}\text{ C}$ . In each case the same spread of values occurred whether the cell was filled with commercial or distilled-water ice and distilled water, or with conductivity-water ice and conductivity water.

When the water in either cell A or cell B was renewed three times with conductivity water according to the method of White,<sup>4</sup> the computed correction for impurity fell to  $0.2$  to  $0.3 \times 10^{-4}^{\circ}\text{ C}$ , approximately the value for the water added.

*Saturation of the Water with Air.* In Tables II and III are given the details and in Table IV a résumé of the results of the calculation of the specific conductances, the composition, and the freezing points of solutions saturated with air at various temperatures and pressures. The computations are based on the ideal-gas law, Dalton's law, Henry's law, and the laws of ideal solutions, and should not be in error by more than 0.5% due to these assumptions. The CO<sub>2</sub> content of laboratory air has been determined on three different occasions, the values falling between 0.034 and 0.036 mol per cent.

Barometric pressure is not under our control but it is always possible to cool the water used in making an ice point cell to  $0^{\circ}\text{ C}$  and saturate it with air. From Table IV it will be seen that when water saturated with air at  $25^{\circ}\text{ C}$  is used a maximum error of  $10 \times 10^{-4}^{\circ}\text{ C}$  may result, if saturated at  $5^{\circ}\text{ C}$ , an error of  $3 \times 10^{-4}^{\circ}\text{ C}$ .

*Conclusion.* The temperature  $t^{\circ}\text{ C}$  in an ice point cell is given by the relation.

$$t = -1.29 \times 10^{-5}(p - 700) - 0.072 \times 10^{-4}L - 42 \quad (L = 0.9 \times 10^{-4}) \quad (5)$$

where the water used in the cell has been saturated with air at  $0^\circ\text{C}$  and a barometric pressure of  $p$  mm,  $h$  is the distance below the surface of the water in mm, and  $L$  is the specific conductance in ohms $^{-1}$  cm $^{-1}$  of the water in the cell measured at  $10^\circ\text{C}$ . If  $L$  is measured at  $0^\circ\text{C}$  the last term of Eq. (5) should read  $55(L - 0.7 \times 10^{-4})$ . The conductance correction is uncertain to 10% and hence should not exceed  $5 \times 10^{-4}^\circ\text{C}$  ( $L = 13 \times 10^{-4}$ ).

When the corrections and implications of Eq. (5) are not taken into consideration, the variations in the indicated temperatures in an ice point cell may be of the order of (a)  $5 \times 10^{-4}^\circ\text{C}$  for variations in the barometric pressure, (b)  $1 \times 10^{-4}^\circ\text{C}$  for variations in depth of immersion of thermometer, (c)  $10 \times 10^{-4}^\circ\text{C}$  for impurities introduced in shaving the ice, and (d)  $10 \times 10^{-4}^\circ\text{C}$  for lack of saturation of the water with air at  $0^\circ\text{C}$  a total of about  $25 \times 10^{-4}^\circ\text{C}$ . In addition there may be a constant error as large or larger than this value due to conditions which, though fairly constant, deviate considerably from standard. A constant temperature in the ice point cell is no guarantee that the temperature is  $0^\circ\text{C}$ .

A second cause of variation in the indicated temperature of the ice point may be in the thermometer itself. The ice point resistance of a well constructed and properly annealed platinum resistance thermometer has changed by an amount equivalent to  $10 \times 10^{-4}^\circ\text{C}$  at the ice point when heated to the sulphur boiling point for as short a time as twelve hours, whereas when used continually at the steam point for three months the ice point resistance has changed by an amount equivalent to  $5 \times 10^{-4}^\circ\text{C}$ . These effects were not due to variation in the temperature in the ice point cell but to real changes in the properties of the thermometer.

Our experience extending over a period of many years with the reproducibility of temperature in ice point cells is summarized in Table V. Method 6 was used for the experimental portion of the work described in the present paper. Method 3, 4, or 5 is used at present for the determination of the ice point of platinum resistance thermometers; in all three the temperature is constant within the precision of the thermometry. Methods 1 and 2 were used previously. Occasionally an indicated ice point will drop by as much as  $50 \times 10^{-4}^\circ\text{C}$ , such a change is always correlated with a very positive test for chlorides in the distilled water used.

When care is used in preparing an ice point cell and when the proper corrections are applied, the ice point can be reproduced to  $0.5 \times 10^{-4}^\circ\text{C}$ .

### 3 VARIABLES AFFECTING THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

*Pressure.* A triple-point cell can be filled with water so free from dissolved air that the pressure of the residual permanent gases is entirely negligible. The lowering of temperature,  $-\Delta t^\circ \text{C}$ , of equilibrium between ice and water at a distance  $H$  mm below the surface of the water is<sup>14</sup>

$$-\Delta t = 0.072 \times 10^{-6}H \quad (6)$$

*Purity of the Ice and Water.* There should be no dissolved  $\text{CO}_2$  in a properly filled triple-point cell. The ice, frozen in the cell, should be of exceptional purity. There is however always some impurity in the water and this increases slowly with time due to solution of the components of glass. Moser<sup>2</sup> found that the specific conductance at  $18^\circ \text{C}$  of the water in a triple-point cell was  $0.3 \times 10^{-6}$  ohms<sup>-1</sup> cm<sup>-1</sup> at the end of several days and after several months the specific conductance was  $0.7 \times 10^{-6}$  when the cell was made of Jena 59<sup>III</sup> glass and  $1.5 \times 10^{-6}$  when of 16<sup>III</sup> glass. In our cell, which was made of pyrex glass, the water had a specific conductance of  $0.7 \times 10^{-6}$  at  $10^\circ \text{C}$  after two months for one filling and  $0.8 \times 10^{-6}$  after two months for another filling. After the third filling the cell was not opened until twenty months had elapsed, when the specific conductance was found to be  $0.8 \times 10^{-6}$ . This result seems to indicate that the impurity present is not due to the progressive solution of the glass. We shall assume the impurity to have the same effect as sodium chloride.

The lowering of the temperature,  $-\Delta t^\circ \text{C}$ , of the triple-point due to impurities in the water is<sup>14</sup>

$$-\Delta t = 42(L - 0.02 \times 10^{-6}), \quad (7)$$

where  $L$  is the specific conductance of the water in the cell measured at  $10^\circ \text{C}$  and  $0.02 \times 10^{-6}$  is the specific conductance of pure water (negligible). For a specific conductance of  $0.7$  to  $0.8 \times 10^{-6}$  the correction is  $-0.3 \times 10^{-4}^\circ \text{C}$ .

*Thickness of the Ice Film.* Neither Moser nor we found any measurable effect due to the thickness of the ice film.

*Radiation and Conduction.* It is usual practice to fill the re-entrant tube of the triple-point cell with mercury in order to increase heat transfer to the thermometer. Heat leaking downward along the thermometer can be made negligible by immersing the entire triple-point tube and part of the thermometer stem in an ice bath.

We found a slight effect, about  $0.3 \times 10^{-4}$  °C, due to radiation. This was eliminated by wrapping the ice bath around the triple-point cell with aluminum foil.

*Conclusion* The temperature  $t$  °C in a triple-point cell is

$$t = 0.00980 - 0.072 \times 10^{-3} H - 42L \quad (8)$$

where 0.0098° C is the triple-point temperature of water,  $H$  the distance below the surface of the water in mm and  $L$  the specific conductance of the water in the cell, measured at 10° C. The conductance correction is uncertain to 30% and hence should not exceed  $1.5 \times 10^{-4}$  °C ( $L = 4 \times 10^{-6}$ ).

The experience of Moser<sup>2</sup> and ourselves shows that it is a relatively easy matter to fill a triple-point cell with water by distillation in vacuo so that the residual air has a negligible effect from the stand-point both of pressure and its solution in the water. When proper glasses are used in the construction of the cell, the specific conductance of the water is below  $1 \times 10^{-4}$  after twenty months, which corresponds to a correction of  $-0.4 \times 10^{-4}$  °C.

Under proper conditions the triple-point of water can be reproduced to  $0.5 \times 10^{-4}$  °C.

#### 4 COMPUTATION OF THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

If we assume that the effect of pressure and of the air dissolved in the water act independently, the computation of the temperature of the triple-point of water is readily made. The effect of an increase of pressure from the triple-point pressure (4.6 mm) to 760 mm can be evaluated from the Clapeyron equation:

$$\begin{aligned} \Delta t &= T(v_w - v_i)\Delta p/\Delta H \\ &= \frac{273.16(1.00013 - 1.09075)755.4 \times 1.01325 \times 10^6}{333.6 \times 10^7 \times 760} \\ &= -0.00747^\circ \text{C} \end{aligned} \quad (9)$$

where the uncertainty is  $0.5 \times 10^{-4}$  °C due to the uncertainty in the density of ice,  $0.9168 \pm 0.0005$  gms per milliliter, and in the heat of fusion of ice,  $333.6 \pm 0.33$  joules per gram.<sup>8</sup> The value obtained by Moser<sup>2</sup> is  $-0.00743 \pm 0.00005$  °C. The effect of saturation of the water with air at a total pressure of one atmosphere is

$$\Delta t = -1.858 \times 0.001313 = -0.00244^\circ \text{C} \quad (10)$$

<sup>8</sup> International Critical Tables, Vol. 3, p. 43 (1928), and Vol. 5, p. 131 (1929).

where the value 0.001313 comes from Table III. The uncertainty is  $0.3 \times 10^{-4}^{\circ}\text{C}$

Thus the computed value of the triple-point temperature of water is  $+0.0099 \pm 0.0001^{\circ}\text{C}$

### 5 MEASUREMENT OF THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

*The Apparatus.* A sketch of the apparatus is shown in Fig. 1. The 48 junction copper (No. 36) constantan (No. 30) thermocouple *A* was divided into 8 groups of 6 junctions each similar to that of Scatchard, Jones, and Prentiss.<sup>6</sup> The binding posts were of copper. The wires were enclosed in a vacuum-tight nickel case filled with dry nitrogen at one atmosphere pressure. The wires were from the same spools as those used by Scatchard and Benedict,<sup>8</sup> and we employed their equation for converting electromotive force into temperature.

$$\Delta t^{\circ}\text{C} = 5.37931 \times 10^{-4}E + 0.2905 \times 10^{-8}E^2 + 0.1413 \times 10^{-14}E^3 + 0.141 \times 10^{-18}E^4 \quad (11)$$

where *E* is in microvolts. We checked this equation for our thermocouple to 0.03% for temperature differences of 2.8 to 3.8° C by replacing the triple-point cell with one similar to the ice point cell filled with shaved ice and a sodium chloride solution. The calibration was made against a platinum resistance thermometer in the manner described by Scatchard, Jones, and Prentiss.<sup>6</sup>

The triple-point cell *B* was similar to that used by Moser.<sup>2</sup> It was made of pyrex glass. The thermocouple was inserted into the re-entrant tube through a rubber stopper and was surrounded by mercury for a distance of 15.5 cm. The cell was steamed out for ten hours, boiled with a 1:1 mixture of concentrated sulphuric and nitric acids, and rinsed many times with distilled and conductivity water. It was sealed in an inverted position to the filling apparatus which contained no stopcocks. Conductivity water was treated with barium hydroxide and the solution poured into the first of two distilling flasks which formed part of the filling apparatus. The water was distilled to the second flask through a spray trap with violent boiling, the system being evacuated by means of a mercury diffusion pump protected by two water traps, the second immersed in liquid air. The first flask was sealed off from the system and the water distilled more slowly into the triple-point tube. In the final distillation

<sup>6</sup> G. Scatchard and M. Allen Benedict, J. Am. Chem. Soc., 58, 837 (1936).

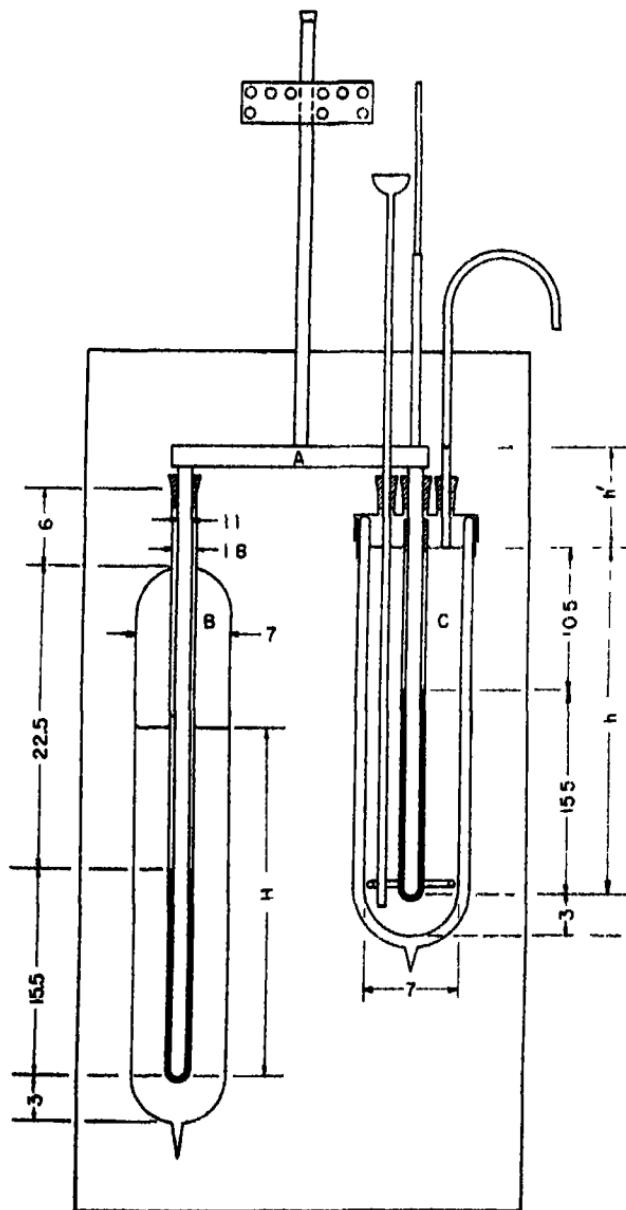


FIG. 1.—Sketch of the apparatus Dimensions are in centimeters

the pressure read near the diffusion pump did not exceed  $10^{-4}$  mm of mercury. Three separate fillings of the cell were made. For the first two the specific conductances of the water after two months was  $0.7$  to  $0.8 \times 10^{-6}$  ohms $^{-1}$  cm $^{-1}$ , for the third, the specific conductance of the water after twenty months was  $0.8 \times 10^{-6}$ .

The ice point cell C was a silvered pyrex Dewar tube fitted with a brass top made water-tight by rubber tape. The top carried four brass tubes through which were inserted one arm of the thermocouple, a tube for the introduction of water, a tube for the removal of water, and a tube carrying a glass stirrer (shown behind the thermocouple in Fig 1). The exit tube and the tube carrying the stirrer projected below the top so that the water in the cell did not come in contact with the metal. The arm of the thermocouple was surrounded by a glass tube from the same piece as the re-entrant tube of the triple point cell, the annular space being filled with mercury for a distance of 15.5 cm.

The entire apparatus was immersed in a bath of cracked commercial ice (1 cm on a side) and distilled water. The large glass vessel was covered with aluminum foil.

*The Measurements.* The triple-point cell was placed in an ice bath and a long glass tube slightly smaller in diameter than the arm of the thermocouple inserted into the mercury well. Liquid ammonia was blown into the tube until a layer of ice  $\frac{1}{8}$  to  $\frac{1}{4}$  inch was frozen around the re-entrant tube. When the surface of the mercury is at the same level as that of the water, super-cooling occurs, when the mercury surface is below that of the water, the freezing proceeds more smoothly.

The ice point cell was filled with a mixture of shaved ice and conductivity water. The water was stored in an ice-chest overnight, and just before use was cooled to  $0^\circ\text{C}$  by the addition of pieces of washed ice about 2 cm on a side and saturated with air by frequent vigorous shaking over a period of one-half hour.

The apparatus was assembled and surrounded by an ice-water mixture. After about one-half hour measurement of the electromotive force of the thermocouple was begun. We found no difference within  $0.2 \times 10^{-4}^\circ\text{C}$  between the values obtained when the mixture in the ice point cell was stirred continuously or when stirred for 30 seconds, the stirring stopped, and the reading made immediately afterwards. When the mixture was not stirred over a period of five minutes the temperature was high by about  $0.5 \times 10^{-4}^\circ\text{C}$  which may be within the experimental error. We adopted the method of intermittent stirring for all of our measurements.

In each run from 6 to 15 readings of electromotive force were made, the water in the ice point cell replaced by pouring air-saturated water cooled to  $0^{\circ}\text{C}$  down the thistle tube and another set of electromotive force readings made, and this process repeated three or four times. The water removed from the cell was stored in stoppered flasks immersed in ice for the determination of specific conductance which was measured at  $10^{\circ}\text{C}$ , as described in Section 2.

After the completion of two series of runs the triple-point cell was opened and the specific conductance of the water at  $10^{\circ}\text{C}$  immediately determined. In the case of Run 5 the cell was not opened until twenty months after the completion of the measurements.

*Corrections.* Each arm of the thermocouple is surrounded by mercury in the same manner, so that it is proper to measure distances of immersion from the bottom of the arm in each cell. The temperature  $t_{ic}$  in the ice point cell is

$$t_{ic} = -1.29 \times 10^{-6}(p - 760) - 0.072 \times 10^{-6}(h + h') - \\ 12(L_i - 0.9 \times 10^{-6}), \quad (12)$$

and the temperature  $t_{tp}$  in the triple point cell is

$$t_{tp} = t_{ic} - 0.072 \times 10^{-6}H - 42L_{tp}, \quad (13)$$

where  $p$  is the barometric pressure at which the water was air-saturated,  $h$ ,  $h'$ , and  $H$  are heads of water in mm (see Fig. 1),  $L_{ic}$  and  $L_{tp}$  are the specific conductances at  $10^{\circ}\text{C}$  of the water in the ice point cell and triple-point cell, respectively, and  $t_{tp}$  is the true triple-point temperature of water.

Let  $\Theta$  be the measured temperature difference  $t_{tp} - t_{ic}$ . Then

$$t_{tp} = \Theta - 1.29 \times 10^{-6}(p - 760) - 0.072 \times 10^{-6}(h + h' - H) - \\ 42(L_i - 0.9 \times 10^{-6} - L_{ic}) \quad (14)$$

*Data.* The data are given in Table VI. Three fillings of the triple-point tube were made. For the third, the specific conductance of the water was taken to be the same as for the second, since this cell was not opened until twenty months after the experimental work was completed. In the third, fourth, and fifth runs the specific conductance of the water from the ice point cell was not determined for every renewal, since the values all lay between  $1.3$  and  $1.4 \times 10^{-6}$  ohms $^{-1}$  cm. $^{-1}$ .

The final value for the triple-point of water is  $0.00980 \pm 0.00005^{\circ}\text{C}$

## 6 SUMMARY

The temperature  $t^{\circ}\text{C}$  in an ice point cell at a distance  $h$  mm below the surface of the water is

$$t^{\circ}\text{C} = -1.29 \times 10^{-4}(p - 700) - 0.072 \times 10^{-4}h - \\ 42(L - 0.9 \times 10^{-4}),$$

where the water used in preparing the cell has been saturated with air at  $0^{\circ}\text{C}$  and a barometric pressure of  $p$  mm and  $L$  is the specific conductance of the water measured at  $10^{\circ}\text{C}$ . The saturation of the air at  $0^{\circ}\text{C}$  and the application of the corrections for barometric pressure and depth are necessary if errors of the order of  $0.002^{\circ}\text{C}$  are important. The conductance correction is uncertain to 10% and should be kept small. With some care in the preparation of the cell and when the corrections for barometric pressure and depth of immersion are applied, temperatures reproducible to  $3 \times 10^{-4}^{\circ}\text{C}$  can be obtained; when the White method of replacing the water in the cell is used the reproducibility is  $0.5 \times 10^{-4}^{\circ}\text{C}$ .

The temperature  $t^{\circ}\text{C}$  in a triple-point cell at a distance  $H$  mm below the surface of the water is

$$t^{\circ}\text{C} = 0.00980 - 0.072 \times 10^{-4}h - 42L$$

where  $0.00980 \pm 0.00005^{\circ}\text{C}$  is the triple-point temperature of water and  $L$  the specific conductance of the water in the cell measured at  $10^{\circ}\text{C}$ . The conductance correction is uncertain to 30%. The temperature in a triple-point cell can be reproduced to  $0.5 \times 10^{-4}^{\circ}\text{C}$ . The specific conductance of the water from a pyrex glass cell was  $0.7 \times 10^{-4}$  and  $0.8 \times 10^{-4}$  ohm $^{-1}$  cm $^{-1}$  after two months for two separate fillings and  $0.8 \times 10^{-4}$  after twenty months for a third filling.

The computed value of the triple-point of water is  $0.0099 \pm 0.0001^{\circ}\text{C}$ , the measured value is  $0.00981 \pm 0.00005^{\circ}\text{C}$ .

CAMBRIDGE, MASSACHUSETTS

TABLE I

## CONDUCTANCE OF WATER FROM VARIOUS SOURCES AND CORRESPONDING COMPUTED FREEZING POINT LOWERING DUE TO IMPURITIES

$$-\Delta t = \text{Freezing point lowering} = 42 (L - 0.9 \times 10^{-4})$$

Source of water	Spec Cond at 10°C	Freezing Pt Lowering
	$L \times 10^4$ , ohms $^{-1}$ cm $^{-1}$	$-\Delta t \times 10^4$ , °C
Conductivity water fresh from still	0.7	
Conductivity water air-saturated at 0°C	1.3	0.2
Melted conductivity-water ice	0.9	
Distilled water from tap	1.4	
Distilled water air-saturated at 0°C	1.6	0.3
Melted distilled-water ice	1.5	
Melted commercial ice	2.0	
Water from ice point cell A	15-25	6-10
Water from ice point cell B	4.6	1.3-2.1
Water from cell A or B after third renewal with conductivity water	1.3-1.5	0.2-0.3

All water used in ice point cells was air-saturated at 0°C. The specific conductance of pure water air-saturated at 0°C is  $0.9 \times 10^{-4}$  ohms $^{-1}$  cm $^{-1}$  at 10°C (on the assumption that no CO<sub>2</sub> is lost).

Calculations of freezing point lowering are based on assumption that all impurity is sodium chloride for which equivalent conductance at zero concentration is 89 ohms $^{-1}$  at 10°C.

In the preparation of cell A the ice was handled with the bare hands, for cell B the ice never came in contact with the hands. The same spread of conductances occurred whether the cells were made of commercial ice or distilled-water ice and distilled water, or of conductivity-water ice and conductivity water.

TABLE II  
SPECIFIC CONDUCTANCES OF WATER SATURATED WITH AIR AT VARIOUS TEMPERATURES

$p_{CO_2}$  (mm) = 0.00035 (760 -  $p_w$ )

$p_w$  = vapor pressure of water (mm)

$$[H_2CO_3] = \frac{1000}{18.0154} \left[ \frac{K}{p_{CO_2}} - 1 \right]$$

$$[H^+] = [HCO_3^-] = \sqrt{[H_2CO_3] \times K_1}$$

$$\gamma = \sqrt{K_1(1-\gamma)/[\text{Total } CO_2]}$$

$$L \text{ (Specific conductance, ohms}^{-1}\text{cm}^{-1}) = L_w + \Lambda_w[HCO_3^-] 1000$$

$$K = p_{CO_2} \text{ (mm)} \cdot \text{mol fraction } H_2CO_3 \text{ in solution}$$

$K_1$  = first ionization constant of  $H_2CO_3$   
 $100\gamma$  = % ionization when  $t$  is changed to  $10^\circ C$   
 without gain or loss of  $CO_2$ .  $K_1$  is for  $10^\circ C$  and

[Total  $CO_2$ ] is for  $t^\circ C$   
 $L_w$  = sp cond of pure water at  $t^\circ C$

$\Lambda_w$  = limiting equivalent conductance of  $H_2CO_3$  at  
 $t^\circ C$

Temp $t^\circ C$	$p_{CO_2}$ mm	$K \times 10^{-4}$	$K_1 \times 10^{10}$	$\Lambda_w$ <sup>a</sup>	$L_w \times 10^8$	$[H_2CO_3]$	$[H^+] = [HCO_3^-]$ mols $\times 10^8$ 1000 gms water	$[\text{Total } CO_2]$	$[\text{Total } Solute]$	% Ionization		$L \times 10^8$	$When t is changed to 10^\circ C without gain or loss of CO_2$	$100\gamma$	$L \times 10^8$
										$L \times 10^8$	$When t is changed to 10^\circ C$				
0	0.264	0.5526	2.61	248	0.01	26.5	2.63	29.1	31.8	9.0	0.66	10.2	0.93		
5	0.264	0.6863	3.00	278	0.02	22.0	2.57	24.6	27.1	10.4	7.3	11.1	8.6		
10	0.263	0.7915	3.38	307	0.02	18.4	2.49	20.9	23.4	11.9	7.8	11.9	7.8		
25	0.258	1.243	4.31	394	0.06	11.5	2.23	13.7	16.0	16.3	9.4	14.5	6.3		

<sup>a</sup> Bohr, see International Critical Tables, Vol 3, p 260 (1928)

<sup>b</sup> T. Sheidlovsky and D. A. MacInnes, J Am Chem Soc, 57, 1705 (1935)

TABLE III  
COMPOSITION OF WATER SATURATED WITH AIR AT VARIOUS TEMPERATURES

Composition of dry air<sup>a</sup> 78.025 mol % N<sub>2</sub>, 20.99 mol % O<sub>2</sub>, 0.94 mol % A, 0.01 mol % H<sub>2</sub>, 0.035 mol % CO<sub>2</sub>  
 $p_A(\text{mm}) = 0.01 \times \text{mol \% A} (760 - p_v)$

$$\text{Mols A/1000 gms water} = \frac{1000}{18.0154 \left( \frac{p_A}{p_A(\text{mm})} - 1 \right)}$$

$$K_A = p_A (\text{mm}) / \text{mol fraction A in solution}$$

Gas	Partial Pressures (mm) in air saturated with water vapor at $t^\circ\text{C}$			Reference	Henry's Law Constant $K \times 10^{-7n}$			Moles Solute $\times 10^6$ per 1000 gms water at $t^\circ\text{C}$				
	0°	5°	10°		23.75	W	4.089	4.609	5.168	6.686	800	708
H <sub>2</sub> O	4.59	6.55	9.21	23.75	W	4.077	4.572	5.074	6.435	802	714	641
N <sub>2</sub>	59.41	58.78	58.50	57.446	F	1.934	2.205	2.486	3.314	455	398	352
O <sub>2</sub>	158.56	158.15	157.59	154.54	W	1.921	2.190	2.460	3.265	458	401	356
A	7.10	7.08	7.06	6.92	W	1.79	2.02	2.25	2.92	22	19	17
H <sub>2</sub>	.08	.08	.08	.07	E	1.635	1.861	2.089	2.708	24	21	19
CO <sub>2</sub>	264	264	263	258	T	4.401	4.623	4.834	5.374	0	0	0
						4.391	4.587	4.778	5.286	0	0	0
									32	27	23	16
									Total (W)	1309	1152	1021
									Total (F, E, T)	1316	1163	1039
									Total (Average)	1313	1158	1030

<sup>a</sup> International Critical Tables, Vol 1, p 393 (1926)

<sup>b</sup> International Critical Tables Vol 3, p 255 (1928)

Values adjusted for 0.035 mol % CO<sub>2</sub>  
 W = Winkler, F = Fox, T = Tumofeev, E = Estreicher

TABLE IV

FREEZING POINT OF WATER SATURATED WITH AIR AT VARIOUS TEMPERATURES  
AND AT A TOTAL PRESSURE OF 760 MM

Total mols solute/1000 gms water air-saturated at total pressure  $p = 760$  mm  
are given in Table III

$\Theta^\circ C$  = freezing point of solution =  $1.858 (0.001313 - \text{total mols solute}/1000$   
gms water)

Specific conductances are from Table II

Temp of Saturation of water with air	Total Mois of solute at $p = 760$ mm	Freezing Point ( $p = 760$ mm )	Specific Conductance of solution at $10^\circ C$
$t^\circ C$	mois/1000 gms water	$\Theta^\circ C$	$\text{ohms}^{-1}\text{cm}^{-1}$
(1)	(2)	(3)	(4)
0	0.001313	0.0	$0.9 \times 10^{-6}$
5	0.001158	+0.00029	$0.9 \times 10^{-6}$
10	0.001030	+ 0.0053	$0.8 \times 10^{-6}$
25	0.000777	+ 0.0100	$0.6 \times 10^{-6}$

Note When the water is air-saturated at  $p$  mm instead of 760 mm

$$\text{Total mols solute}/1000 \text{ gms water} = \frac{p - p_w}{760 - p_w} \times \text{value for } 760 \text{ mm}$$

Because of the slight effect of the ionization of  $\text{H}_2\text{CO}_3$ , this equation holds to the number of places given in column (2) of the above table

TABLE V  
OBSERVED VARIATIONS IN ICE POINT CELLS

Barometric correction ( $^{\circ}\text{C}$ ) =  $-1.28 \times 10^{-5} (p - 760)$   
 Immersion correction ( $^{\circ}\text{C}$ ) =  $-0.072 \times 10^{-5} h$   
 Conductance correction ( $^{\circ}\text{C}$ ) =  $-42 (L - 0.9 \times 10^{-4})$   
 $p$  = barometric pressure in mm  
 $h$  = depth of immersion in mm.  
 $L$  = specific conductance ohms $^{-1}$  cm $^{-1}$  of water  
 from cell measured at  $10^{\circ}\text{ C}$

Method	Preparation of Ice Point Cell			Corrections Applied			Spread from maximum to min temp $\Delta T \times 10^4 ^{\circ}\text{C}$		
	Ice	Water	Handling of ice	Air-Saturation at $0^{\circ}\text{C}$	Replacement of water in cell	Barometric	Immersion	Conductance	
1	Commercial	Distilled	By hand	no	no	no	no	no	30
2	Commercial	Distilled	By vessel	no	no	no	no	no	15
3	Distilled water	Distilled	By vessel	yes	no	yes	yes	yes	5
4	Distilled water	Distilled	By vessel	yes	no	yes	yes	no	3
5	Distilled water	Distilled	By vessel	yes	yes	yes	yes	no	1
6	Conductivity water	Conductivity	By vessel	yes	yes	yes	yes	yes	0.5

TABLE VI  
THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

$I\ P$  = ice point       $T\ P$  = triple-point  
 $H$  = distance from bottom of thermocouple tube to water level in  $T\ P$  cell  
 (see Fig. 1)  
 $h + h'$  = distance from bottom of thermocouple tube to water level in  $I\ P$   
 cell (see Fig. 1)

Preparation of $I\ P$ Cell	No of Readings	E M F	$\Theta$	$H$	$h$	$h'$
		microvolts	$^{\circ}\text{C} \times 10^4$	mm	mm	mm
(1)	(2)	(3)	(4)	(5)	(6)	(7)
Run 1      First filling of triple-point cell						
Orig filling	15	19.61	10549	220	260	70
1st renewal	15	18.57	9989	220	260	70
2nd renewal	10	18.47	9936	220	200	70
3rd renewal	13	18.65	10032	220	260	70
Run 2      First filling of triple-point cell						
Orig filling	6	18.95	10194	220	260	130
1st renewal	9	18.52	9962	220	260	0
2nd renewal	8	18.62	10016	220	260	110
3rd renewal	16	18.51	9957	220	260	90
Run 3      Second filling of triple-point cell						
1st renewal	6	18.18	9780	260	260	50
2nd renewal	7	18.23	9806	260	260	50
3rd renewal	6	18.33	9860	260	260	50
4th renewal	7	18.28	9833	260	260	50
Run 4      Second filling of triple-point cell						
1st renewal	6	18.14	9758	260	260	0
2nd renewal	6	18.26	9823	260	260	0
3rd renewal	8	18.19	9785	260	260	0
4th renewal	8	18.03	9699	260	260	0
Run 5      Third filling of triple-point cell						
1st renewal	6	18.27	9828	260	260	20
2nd renewal	7	18.15	9763	260	260	20
3rd renewal	7	18.16	9769	260	260	20
4th renewal	7	18.06	9715	260	260	20

TABLE VI—Continued

## THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

$$\Theta^{\circ}\text{C} = 0.00053793 E$$

Correction for static head ( $^{\circ}\text{C}$ ) =  $-0.00000072 (h + h' - H)$

Correction for barometric pressure ( $^{\circ}\text{C}$ ) =  $-0.0000129 (p - 760)$

$p$  = barometric pressure in mm

Correction for conductance ( $^{\circ}\text{C}$ ) =  $-42 (L_{te} - 0.9 \times 10^{-6} - L_{te})$

Bar	Specific Conductance at $10^{\circ}\text{C}$		Corr for static head	Corr for barom- eter	Corr for conduct- ance	Temp of triple- point
	I P Cell	'I P Cell				
mm	$L_{te} \times 10^6$	$L_{te} \times 10^6$	$^{\circ}\text{C} \times 10^6$	$^{\circ}\text{C} \times 10^6$	$^{\circ}\text{C} \times 10^6$	$^{\circ}\text{C}$
(8)	(9)	(10)	(11)	(12)	(13)	(14)
Commercial ice and conductivity water in ice point cell						
767.0	15.0	0.7	-70	-90	-56.3	0.00982
767.0	1.5	0.7	-79	-90	+4	0.00982
767.0	1.5	0.7	-79	-90	+4	0.00977
764.7	2.6	0.7	-79	-61	-42	0.00985
Conductivity ice and conductivity water in ice point cell						
767.2	6.0	0.7	-122	-93	-185	0.00979
767.2	1.5	0.7	-29	-93	+4	0.00984
767.2	1.5	0.7	-108	-93	+4	0.00982
767.2	1.5	0.7	-94	-93	+4	0.00977
Conductivity ice and conductivity water in ice point cell						
761.0	1.3	0.8	-36	-13	+17	0.00975
760.7	1.3	0.8	-36	-9	+17	0.00978
760.5	1.3	0.8	-36	-6	+17	0.00984
760.5	1.3	0.8	-36	-6	+17	0.00981
Conductivity ice and conductivity water in ice point cell						
756.6	1.4	0.8	0	+44	+13	0.00982
757.0	1.4	0.8	0	+39	+13	0.00988
757.0	1.3	0.8	0	+39	+17	0.00984
757.0	1.3	0.8	0	+39	+17	0.00976
Conductivity ice and conductivity water in ice point cell						
756.2	1.4	0.8	-14	+49	+13	0.00988
756.2	1.4	0.8	-14	+49	+13	0.00981
756.8	1.4	0.8	-14	+54	+13	0.00982
755.6	1.4	0.8	-14	+57	+13	0.00977
Average						0.00981
$\pm 0.00003$						



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**THE RESISTANCE OF NINETEEN METALS  
TO 30,000 Kg/Cm<sup>2</sup>**

**BY P. W. BRIDGMAN**



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INTRODUCTION

The pressure range of the following measurements of electrical resistance, 30,000 kg/cm<sup>2</sup>, is considerably greater than that of my previous measurements. My extreme previous range has been 20,000 kg/cm<sup>2</sup>, realized for half a dozen substances only,<sup>1</sup> and almost all my other former work has been restricted to 12,000.<sup>2</sup> My endeavor in this new work has been to pick out those substances for measurement which previous work suggested would be most significant in this new range. Probably the most significant of the new results are those for the minimum resistance of potassium, and the resistances of the new high pressure polymorphic forms of bismuth, caesium, and barium.

## APPARATUS

The extension of pressure range has been made possible by the development of a new type of apparatus. The fundamental principle of this is the same as that of the apparatus for measuring volume changes and polymorphic transitions up to 50,000,<sup>3</sup> namely the application of pressure externally to the pressure chamber to partially compensate for the effect of the internal pressure. The new apparatus is larger and more complicated than the 50,000 apparatus, the volume of the pressure chamber being 16 cm<sup>3</sup> instead of 0.6 cm<sup>3</sup>. The external pressure on the pressure chamber is produced by the independent action of a second hydraulic press, instead of automatically by the action of the same press which produces the internal pressure. Although the second press makes considerable complication, the advantages of being able to vary independently the external and internal pressure more than compensate.

The method by which external pressure is produced on the pressure chamber is the same as in the 50,000 apparatus, namely the pressure chamber is made slightly conical on the external surface, and this cone is forced into a heavy conical sleeve simultaneously with the production of internal pressure. The restrictions set by the cone demand the use of a second press when the size of the apparatus becomes as great as in this apparatus, for if the external pressure were produced automatically by the thrust on the high pressure piston, the angle of the cone would become so small that friction would prevent satisfactory functioning.

The apparatus is shown schematically in Figure 1, which is drawn very approximately to scale, and a photograph of the assembly in Figure 2. A good deal of time was spent in the development of this apparatus, and since there are a number of features which are not entirely straightforward, it will pay to describe the construction in some detail.

Figure 1 shows the double-headed press. The piston of the lower press, with which pressure is produced on the outside of the pressure chamber, is 6 inches in diameter and has a 1.5 inch stroke. The piston of the upper press, which drives the plunger producing the internal pressure, is 3.5 inches in diameter and has a stroke of 4 inches. These two presses are actuated by two hand pumps of my conventional design, capable of exerting a pressure of 15,000 lb/in<sup>2</sup>. Valves and couplings in the lines from pumps to presses enable the pumps to be entirely cut out if necessary, after pressure has been reached, and pressure maintained constant without motion of the pistons. A

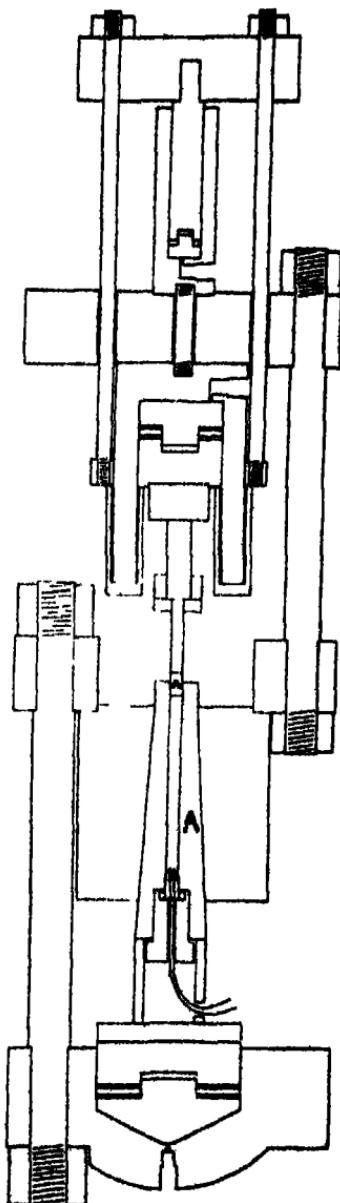


FIGURE 1 Section of the general assembly. The two working presses use three tie rods each, shown in the figures as one. The small cylinder at the top serves to restore the middle piston to its initial position, and plays only a subsidiary part.

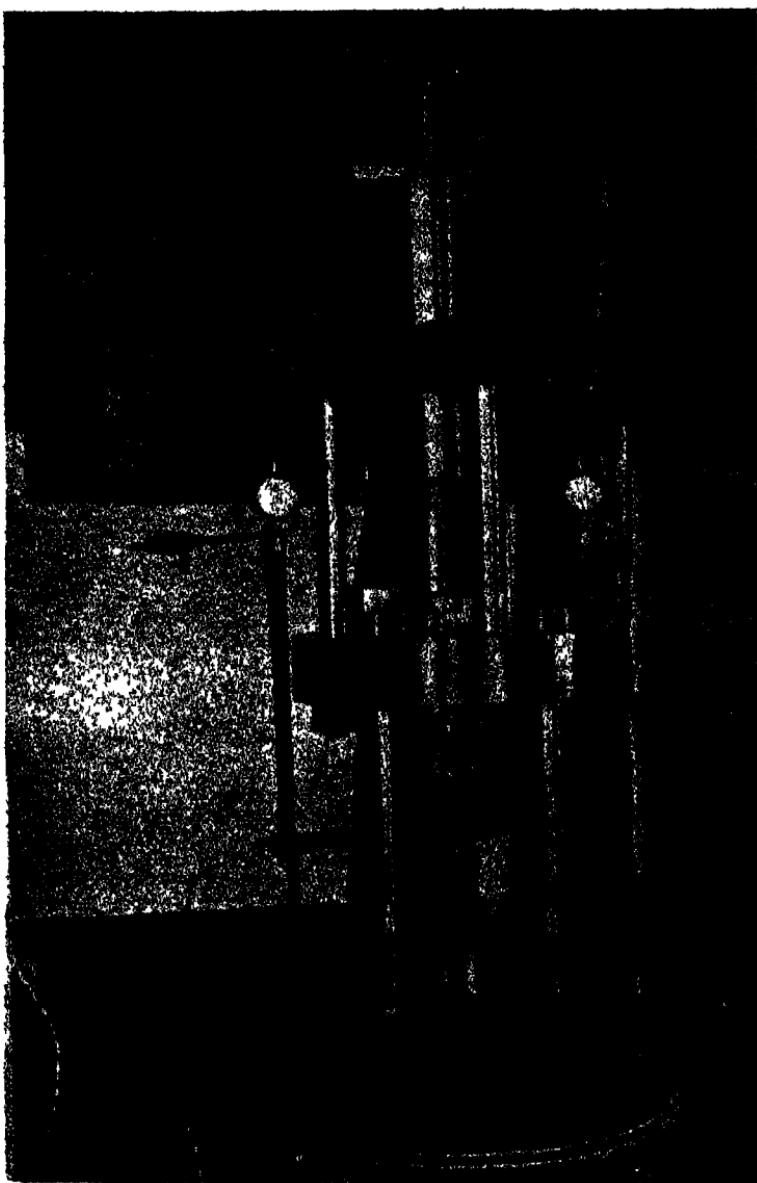


FIGURE 2 Photograph of the complete assembly, ready to lower into the oil bath

third hand pump is also necessary for operation, this pump produces initial pressure up to 2,000 kg/cm<sup>2</sup> through a by-pass at the upper end of the pressure chamber by means of an intensifier of my standard design. The only respect in which the priming arrangements differ from the usual ones is in the small size of the connecting tube, which is of nickel, 0.125 inches outside diameter and 0.015 inches inside diameter. This small size was necessary in order to attain the necessary flexibility and ease of handling.

The high pressure chamber, shown at A, is made of "Solar" steel or of "S M" steel, two somewhat similar steels made by the Carpenter Steel Co. The analyses and heat treatment have been given in previous papers.<sup>4</sup> In addition to great strength and elongation, another advantage of these steels is that they can be enlarged with a reamer without glazing the reamer when in a state of hardness materially greater than that possible with most other steels. In use, there is some wear of the inner surface of the cylinder, so that it is necessary to re-ream the hole from time to time. For this purpose there are four reamers of high speed steel, respectively of 0.490, 0.500, 0.510, and 0.520 inches diameter. All the measurements in the following were made with a single high pressure chamber, starting at 0.490 and ending at 0.520. I am not planning to enlarge the hole further, but shall discard the chamber when the present size, 0.520, becomes too much worn.

The pistons are made of carboloy, for which I am much indebted to the Carboloy Co of America, and Dr Zay Jeffries. Because the internal diameter of the pressure chamber may actually decrease when external pressure is applied, it is necessary, in order to avoid pinching the piston into the cylinder, to make the diameter of the carboloy piston less than the diameter of the hole. A clearance of 0.005 inches has proved adequate. Four carboloy pistons are therefore required, respectively 0.485, 0.495, 0.505, and 0.515 inches diameter. In spite of the fact that 30,000 is much less than the crushing strength of carboloy, which I have found to be as high as 65,000, the pistons will not stand up indefinitely, but very soon fine longitudinal cracks appear, which slowly increase in size and number, until eventually the piston fails by splitting into longitudinal prisms. Failure begins at the lower end of the piston, where it is in contact with the moving plug. Failure might also begin at the top end if it were not prevented there by a very heavy hardened steel collar, with a 0.5° taper, forced around the upper end of the piston. Two grades of carboloy piston were tried. The first grade, number 905, has the highest compressive strength of

any of the grades of carboloy, and is the variety used in my work to 50,000. The second grade, number 883, has a lower compressive strength, but a higher strength in tension, that is, it permits a greater elongation without rupture. For this reason it seemed that longitudinal cracks might be less likely to form. As a matter of fact, not much difference could be found between the two grades for present purposes.

In order to permit an approximate evaluation of the distortion of the pistons under pressure, I made a rough determination of Young's modulus and Poisson's ratio. These were respectively, for grades 905 and 883,  $E = 99 \times 10^6$  lb/in<sup>2</sup>,  $\sigma = 0.267$ , and  $E = 92 \times 10^6$ ,  $\sigma = 0.359$ .  $\sigma$  was measured directly from the lateral expansion under compressive load.  $E$  has been measured before at the Bureau of Standards for carboloy, and these extraordinarily high values checked Poisson's ratio apparently has not been previously measured. The great difference for the two grades was a surprise. There seemed nothing obviously wrong with either measurement. Perhaps the material is not very homogeneous. In any event, the distortions of the piston up to the extreme pressures reached here, 30,000 kg/cm<sup>2</sup>, are small, the piston shortens by 0.5 per cent, and expands laterally by less than 0.001 inch, well within the clearance limit.

The leak-proof plug pushed by the carboloy piston is of the mushroom "unsupported area" type which I have used in all my work. 30,000 kg/cm<sup>2</sup> is about the limit which such a plug will stand in the best grade of steel that I have been able to find, failure being by pinching off the stem of the mushroom. A plug can seldom be used for more than three or four excursions to 30,000, and in fact many times pinching off has progressed to such an extent after two applications that the plug has been discarded. It was only by special design that it was possible to carry the plug to this pressure at all. The construction is shown in Figure 3. The plug is made of "Seminole Medium" steel of the Ludlum Steel Co., quenched into oil instead of into water, and drawn to a Rockwell C hardness of 59. The stem of the mushroom is made shorter and smaller in diameter than usual, in this way cutting down the excess pressure in the packing. Packing only 0.125 inches thick is used, this makes the stressed part of the stem so short that it receives effective support from the massive head. "Duprene" packing is used instead of soft rubber. The packing itself is prevented from leaking by the conical rings shown in Figure 3. The rings are made of Cr Va steel, either untreated or else hardened and drawn back nearly to the initial softness. Ordinary mild

steel is unsuitable for these rings because it extrudes between mushroom and cylinder walls. The piece *T*, by which the mushroom is pushed by the carboloy piston, is made of "Teton" steel, left glass hard. Surprisingly, no trouble was experienced from the upsetting of this, doubtless because of its shortness and the frictional support of the ends.

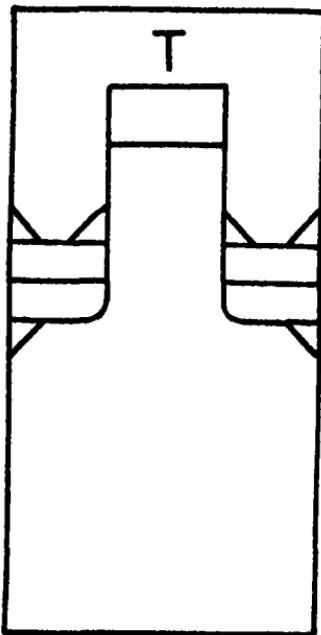


FIGURE 3. Details of the moving plug

The outside of the pressure vessel *A* (Figure 1) was ground to a taper of 1 inch (on the diameter) per foot of length. The smaller the taper, the larger the external pressure on the external surface attainable with a given thrust. The smaller the taper the better, therefore, except for the limitations imposed by friction. My first experiments with this apparatus were made with a taper of 1 125 inches per foot. Comparative studies of the friction effects with the two tapers led to the conclusion that the smaller taper was superior.

The conical collar supporting the pressure chamber on the outside has to support an internal pressure of close to the maximum allowed

by its tensile strength, so that it is important to get the best construction. A number of these collars were ruptured before success was attained. The total thickness of the collar is 6.375 inches, it was made from three discs, each 2.125 inches thick. The advantage in making it in three discs is that thus each disc is thin enough to receive nearly the maximum benefit from heat treatment throughout its entire mass. The discs were made of "Solar" steel, the central hole forged into the disc, and then the disc hammered around a tup through the central hole, so that there was some working of the fibres circumferentially. This circumferential forging proved essential, without it the discs break. The discs were hardened, drawn to a Rockwell C hardness of 53, ground flat and parallel on both faces, and the central hole ground to the required taper, but a little smaller than final dimensions. Each ring was then stretched separately by forcing into it a solid conical piece of the same taper as the pressure chamber, until a permanent stretch of the order of 5 per cent was produced. With suitable allowance for friction, the maximum pressure reached during the stretching process was about  $15,000 \text{ kg/cm}^2$ . The elastic distortion of the ring corresponded to an elastic displacement of the internal cone along its axis of 0.4 inches at the maximum. The three rings having been separately stretched, they were then clamped together, and the hole ground to final dimensions in all three simultaneously. I have had only one failure of a ring in the final apparatus.

Lubrication between the pressure chamber and the collar was by the same method as used in the 50,000 apparatus, namely a paste of graphite, water and glycerine, smeared on both sides of a sheet of 0.002 inch lead interposed between collar and cone. The details have been described in the preceding paper,<sup>5</sup> as also the method of evaluating friction by measuring the axial displacement of the cone as a function of thrust with increasing and decreasing pressure. A quantitative study was made in this way of the frictional effects in this apparatus, and the effective over-all friction found to be of the order of 5 per cent. That is, if the thrust on the 6 inch piston was such as to indicate by a calculation neglecting friction that the external pressure on the pressure chamber was  $10,000 \text{ kg/cm}^2$ , the actual external pressure was 9,500.

During the actual measurements, at the top pressure of 30,000, very nearly the maximum pressure of which the apparatus was capable was applied to the 6 inch piston, namely  $14,500 \text{ lb/in}^2$ . The effective thrust exerted by the 6 inch piston is diminished by that exerted by the 3.5 inch piston, since the two pistons oppose each other.

At 30,000 kg/cm<sup>2</sup> the pressure on the 3.5 inch piston was about 10,000 lb/in<sup>2</sup>. Since the ratio of the areas of the two pistons is 0.34, the effective pressure exerted by the 6 inch piston is approximately 11,000 lb/in<sup>2</sup>. Making allowance for friction, this means a pressure of approximately 10,000 kg/cm<sup>2</sup> on the outside of the high pressure cone. In the previous paper will be found the material from which the distortions may be calculated. 10,000 external pressure produces on the inside a contraction numerically equal to the expansion produced by an internal pressure of 15,000. This is an approximate measure of the increase of range made possible by the external pressure. As a matter of fact, in practise the external support seemed to be even more effective than this very rough theory would indicate. The same high pressure chamber was used for all the measurements reported in the following, representing nearly 50 applications of 30,000. This is in striking contrast to the half dozen or so applications which was the best that could be obtained with the former unsupported cylinder to only 20,000. Furthermore, the high pressure cylinder did not receive for this work any preliminary stretching, such as has always been necessary before. It was a very great convenience to be able to dispense with the preliminary stretching, which becomes very awkward if the entire bore has to be stretched uniformly.

It appears, therefore, that by the use of external support as in this apparatus, the weakest part is no longer the pressure chamber itself, but failure occurs at other parts of the apparatus. The limit set by the pinching off of the mushroom stem of the moving plug is not far above 30,000, but the limiting feature in the actual experiments was the insulating plug by which the leads were taken in at the lower end for electrical measurements. There are two major causes of failure in any ordinary type of insulating plug: pinching off of the lead itself, and extrusion of the insulating material through the annular space where the lead leaves the pressure chamber. It is ideally possible to overcome both these weaknesses simultaneously and make a plug that will withstand a single application of any pressure, no matter how high, merely by making the column of insulating material long enough. The frictional resistance to extrusion afforded at the walls of a cylinder increases enormously with the length, the stress at the exit end dropping off exponentially with increasing length. Since it is the stress at the exit end which determines the pinching off and extrusion, these two effects can be easily eliminated if the length is great enough. The difficulty comes when one attempts to apply the pressure a second time. On the first release of pressure, expansion of

the insulator forces the stem to pull itself back through the insulator, which may exert such great friction because of its length that the stem pulls itself in two. If a plug is to be used more than once, some sort of compromise has to be effected, by suitably choosing materials and dimensions, between the friction on increasing pressure, which is advantageous, and friction on decreasing pressure, which is fatal. In the first place it is obviously an advantage that the insulating stem should be of the maximum strength. Tungsten wire would seem indicated for this purpose, it was a great disappointment to find that the fibrous structure of ordinary tungsten wire is so pronounced that under the conditions encountered in these plugs the wire disintegrates into longitudinal fibres. It was necessary, therefore, to return to commercial piano wire. In order to stiffen this beyond its commercial condition, I drew it down from 0.0140 inches to 0.0135 inches through a diamond die. This extra step in the drawing resulted in a very appreciable increase of strength. For the insulator, various materials were tried. Sapphires, which had proved effective to 20,000, were completely fractured by a single excursion to 30,000. Solenhofen limestone, which was, perhaps, first suggested at the Geophysical Laboratory in Washington, in proper combination with mica, proved effective. It is necessary to select a suitable piece of limestone with some care, much of the commercial material is too soft. Recently I have been successful with a construction replacing most of the limestone with steel, suggested by Mr Charles Chase.

The detailed construction of the plug is shown in Figure 4. The steel parts of the plug require care in construction, since  $30,000 \text{ kg/cm}^2$  is pretty close to the limit that any steel, even in the glass hard condition, will support in compression indefinitely without some yield. The steel used was "Teton," drawn to give a Rockwell C hardness of 59. The projecting end was ground to an angle of  $1^\circ$ , and reinforced by being forced into a collar of heat treated Cr Va steel, C. This collar prevented spreading and cracking of the projecting end, which otherwise always took place. The plug carries four insulated leads, one for the manganin gauge and three for the measurement of various resistances by the potentiometer method. The apparatus itself is the common ground of the manganin gauge and the fourth of the potentiometer terminals. I was never able to construct a plug which I could count on to use for more than two excursions to 30,000, this was sufficient for measurements on a single substance at  $30^\circ$  and  $75^\circ$  with a single set-up. Even as it was, the two runs were often not complete. Attempts to use the plug for two more runs were sometimes successful,

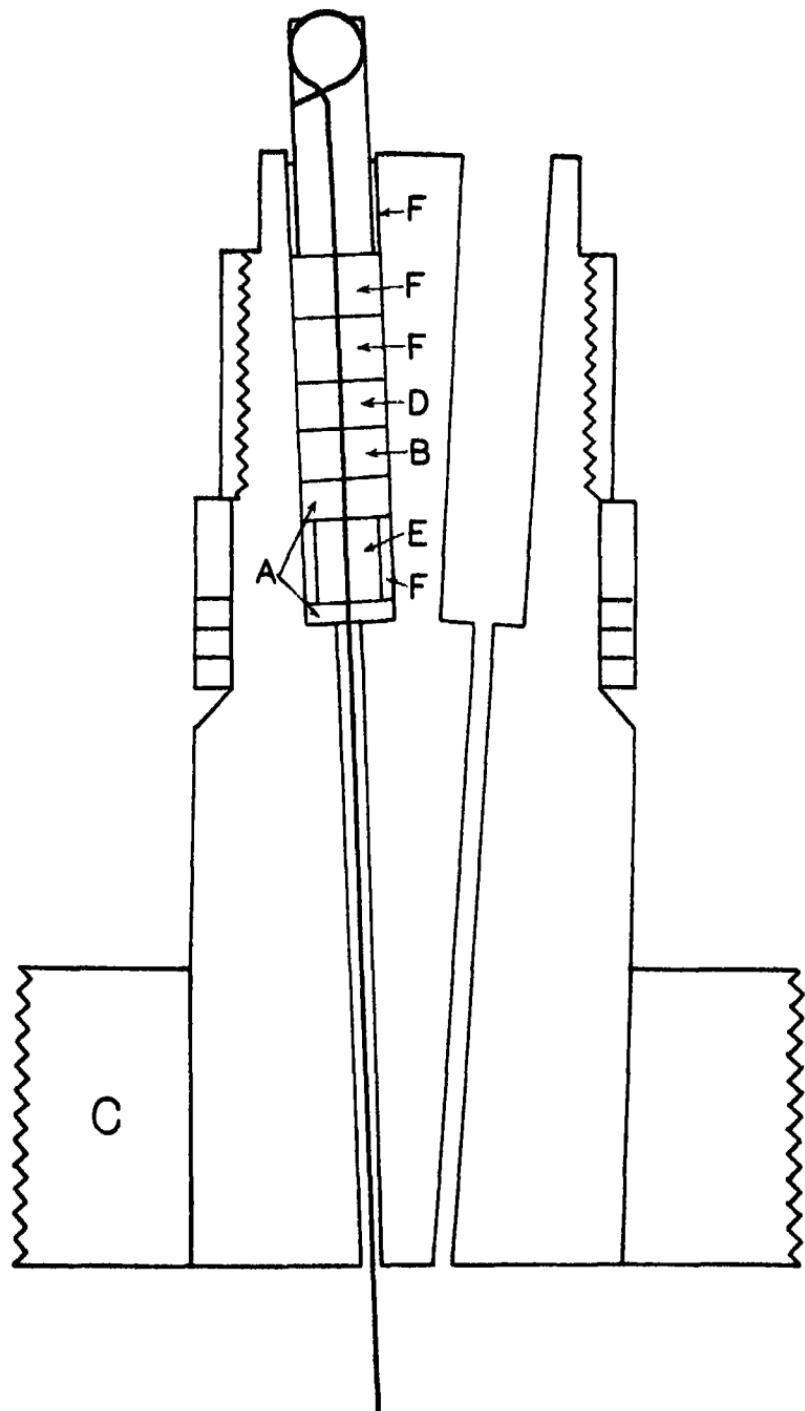


FIGURE 4 Assembly of the insulating plug A, mica, B, soft rubber, D, Duprene, E, hardened steel, F, pipestone

but more often than not one of the four terminals went wrong. The chances of success are obviously much less with four terminals, if only a single terminal had been involved it probably would have been economical to continue with the same plug until it failed, but with four it seemed best to reassemble the plug after two runs with a single substance. Such frequent reassembly of the plug was very time consuming, and it was the limitations imposed by the plug that mainly restricted the amount of data that could be turned out in a given time. Because of this limitation of output, I had to try to choose my materials for measurement so as to give the totally most useful information. This is the reason that some of the data in the following are incomplete. If, for example, a successful run had been made at  $30^{\circ}$ , and then at  $75^{\circ}$  the plug failed, making necessary a new set-up in any event, I usually preferred to make the new set-up with a new substance, leaving the data for the first substance incomplete, hoping to come back to it later, perhaps.

As already intimated, resistance measurements were made at two temperatures  $30^{\circ}$  and  $75^{\circ}$ . Temperature was maintained by putting the entire lower part of the double press, up as far as the carbonyl piston, in a thermostated oil bath. The entire press, which weighs in the neighborhood of 1,000 lb., was handled by a chain hoist, traveling on an I beam attached to the ceiling. The thermostating arrangement was conventional enough, and does not need description. The heating was electrical. The amplitude of the temperature cycle in the bath was seldom as much as  $0.05^{\circ}$ , and the period was of the order of ten minutes at  $75^{\circ}$ . There was no appreciable drift of temperature during a run. Temperature equilibrium is reached only slowly in masses as large as this, and without some device it would have taken an entire day to reach temperature equilibrium before starting a run. The device was adopted, when raising the temperature, of running the temperature of the bath beyond the final temperature, and then allowing it to drop back. It was thus found possible, after some experimenting, to make the change of temperature from  $30^{\circ}$  to  $75^{\circ}$  in from one and one half to two hours. After each increase of pressure it was necessary, as usual, to wait for the heat of compression to be dissipated, but there was nothing unusual in this situation. At the lower pressures readings could be made in from seven to eight minutes after a 5,000 kg increment of pressure. At the higher pressures the thermal conductivity of the pressure transmitting medium had become so much greater that readings could be gathered as fast as the various instruments could be read, a reading perhaps every three or four minutes.

Pressure was measured in terms of the change of resistance of a coil of manganin wire. The manganin resistance has been directly calibrated<sup>6</sup> only to 13,000 kg/cm<sup>2</sup>, up to this pressure, change of resistance is linear in the pressure within 0.1 per cent. The pressures beyond 13,000 had to be extrapolated. There are, however, various indications as to the general goodness of such an extrapolation. There is in the first place the internal evidence of the resistance measurements themselves. An argument from this point of view has already been used in connection with my measurements to 20,000.<sup>7</sup> If the pressures, as determined from the resistances of several different substances, all extrapolate to the same value, then the presumption is that none of the extrapolations is far wrong. In the following will be found data for the resistances of copper, silver, gold, and iron discussed from this point of view. The point of using just these four metals was that they were conveniently available, and their resistances are more nearly linear than that of many other metals, so that extrapolation is less hazardous. Extrapolation of other phenomena than resistance would also give a basis for an estimate of the true pressures. In the following will be found a measurement of the melting pressure of mercury at a temperature of 75°. The melting curve of mercury has previously been followed up to 20°, where the melting pressure is 11,800 kg/cm<sup>2</sup>. Extrapolation of the previous melting curve to 75° by assuming constant second differences (the first vary only slightly, so that the departure from linearity is only slight) indicates a melting pressure of 22,595 at 75° against 22,570 measured with the manganin gauge. Another sort of estimate can be obtained from the melting curve of ice VI. Formerly I had followed this curve up to 21,000 in terms of the manganin gauge,<sup>8</sup> all pressures above 13,000 thus being extrapolated. I have recently redetermined a point on this curve with the 50,000 apparatus, pressure in this is determined by measuring the actual thrust on the piston, that is, it is essentially an absolute gauge determination. At 80° the new melting pressure does not differ from the previous value by more than 200 kg/cm<sup>2</sup>, indicating an error in the manganin gauge at 20,000 or not more than the difference. Finally, it is possible to make what is essentially an absolute calibration of the manganin gauge to 30,000 in terms of the actual thrust on the piston with which pressure is produced. Of course the objection to this method is the insensitiveness due to friction, but within the limits imposed by friction the results should have absolute significance. It turned out, furthermore, that the frictional effects were surprisingly low. The total friction on the 3.5 and the 6 inch

pistons of the press together was less than 3 per cent, determined by pushing first one piston with the other and then inversely. Furthermore, the friction at the high pressure moving plug was much less than in my other apparatus. This was due to a combination of factors. The "Duprene" packing was not as thick as usual, the external pressure on the cylinder prevented the interior from expanding as much as formerly, so that the extrusion of the soft steel rings, with which the "Duprene" was retained, into the annular space between hardened mushroom and cylinder walls was almost negligibly small (this is usually the major source of friction), and the clearance between cylinder walls and carboloy piston was sufficient to remove all friction at this point. Measurements were made of the resistance of the manganin in terms of the pressure on the pistons of the press, taking the means with increasing and decreasing pressure. In the neighborhood of 25,000 the means with increasing and decreasing pressure differed by something of the order of 10 percent, that is, the piston just started to move in at 7,800 lb/in<sup>2</sup> on the 3 5 inch piston, and just started to move out at 7,000. Making a one per cent correction for increase of cross section of the cylinder at 25,000, the piston pressure was 25,300 against a manganin pressure of 25,000. The agreement is better than I had anticipated. All in all, it seems probable to me that the manganin pressure gauge is not in error by more than 1 or 2 per cent, and there is no certain evidence that it is in error at all.

The manganin gauge was constructed of double silk covered wire 0.003 inches in diameter, obtained from Driver Harris Co., and of American manufacture. The wire was from the same spool as the gauges which I have used in various measurements at liquid air temperature.<sup>9</sup> The total resistance of the gauge was about 65 ohms. It was wound as usual non-inductively into a coreless anchor ring, the dimensions being about 6 mm. overall outside diameter, and 3 mm. thickness. It is thus materially smaller than my other gauges, a feature made necessary by the limitations of space. It is so small that in the pressure apparatus it could be mounted on its side between a couple of the terminals of the insulating plug. Calibration was as usual in terms of a single fixed point, the freezing pressure of mercury at 0°C, taken as 7640 kg/cm<sup>2</sup>. Calibrations were made independently at 30° and 75°, the constant is 0.6 per cent greater at 75° than at 30°. The coil was seasoned by a preliminary heat treatment at atmospheric pressure for eight hours a day for seven days to 140°, and then by a couple of preliminary applications of the full 30,000. Whatever the explanation, the seasoning was unusually effective, and the drift of

zero has been conspicuously less than with some of my other gauges.

During the preliminary work with this apparatus a quantitative study was made of a number of features not yet mentioned. (1) The stretch of the tie rods of both the 3.5 and the 6 inch press was determined with increasing and decreasing pressure. (2) The two pistons were directly coupled together and the pressure determined, over the entire range of pressure, which was required by either to push the other, giving in this way the packing friction. (3) The external expansion of the retaining rings was determined as a function of pressure. (4) Finally, the internal contraction of the pressure chamber was determined when it is pushed into the supporting rings by the 6 inch piston, with no internal pressure. There is no need for the purposes of this paper to describe all these measurements in detail, but they had great value in permitting a complete picture of the functioning of the whole assembly.

The pressure liquid was iso-pentane, this has the lowest freezing point of any readily available liquid not boiling below room temperature. One of the routine measurements always made was to record the position of the piston as a function of pressure, the freezing of the iso-pentane would have been shown by a discontinuity in the motion. No such discontinuity was ever found, nor any other evidence of the freezing of the iso-pentane. The iso-pentane was of ordinary commercial grade, obtained from the Eastman Kodak Co. It may be that it contained sufficient impurity to materially depress the freezing point, or possibly freezing was suppressed altogether, although the freezing range may have been entered, because of viscous resistance to formation of the nuclei of the solid phase. Whatever the reason, the failure to freeze was fortunate, and a pleasant surprise.

The actual routine of the measurements does not need much detailed discussion. Usually readings were made at 5,000 intervals up to 30,000, and then with decreasing pressure at 27,500 and at 5,000 intervals thereafter. Practically never was there any perceptible hysteresis. Since the boiling point at atmospheric pressure of iso-pentane is less than 30°, it was not possible to start from dead zero at 30°, but a zero was used of a few hundred kilograms. Extrapolation to zero should introduce no appreciable error. At 75° the pressure of the lowest reading was usually in the neighborhood of 2,000, so that there is perhaps more possibility of zero extrapolation error but it should not be important in any event. The zero of the manganese gauge at 75° was usually checked by completely removing the moving plug and letting the iso-pentane boil out. Sometimes it was possible

to get also the zero of the resistance under investigation under the same conditions, but the temperature sensitivity is much greater than that of the manganin, and the temperature fluctuations in the isopentane vapor were usually too great to permit this.

In addition to the electrical measurements, as a matter of routine, record was always made of the pressure on the 6 inch and the 3.5 inch pistons, the motion of the pressure chamber into its conical collar, and the motion of the carboloy piston. These data were seldom used,<sup>1</sup> but sometimes they proved convenient. Thus it was possible to check at any time the friction of the cone in the collar, this check was made at intervals during the progress of the work, and no progressive change found. From the motion of the carboloy piston it should also be possible to get an approximate value for the compressibility of isopentane.

The detailed data now follow.

#### DETAILED DATA

*Copper, Silver, Gold.* The material on which these measurements were made consisted of the identical coils of my original measurements in 1916. The wire was double silk covered, wound non-inductively on itself into a coreless toroid, with resistances of 41, 24, and 20 ohms respectively. Because of the high resistance, the technique of measuring the resistance was different from that used for the other metals, all of which had a much lower resistance. Fluctuating resistance at the contacts is not a factor when the resistance is as high as this, so that the resistance of these three metals could be measured on the same Carey Foster bridge that was used for the manganin resistance gauge. A bridge measurement of this sort demands only two leads, since the insulating plug had four leads, all four coils, manganin, copper, silver, and gold, were connected to the plug and measurements made on all four at each pressure. One or the other resistance was connected to the bridge through a simple arrangement of mercury switches. The relative measured decrements of resistance of these three metals are thus independent of any failure of perfect reproducibility in the manganin gauge.

These measurements were the first made with the pressure apparatus, and there were various hitches in getting the apparatus to functioning properly, there being trouble from leak, or short or open circuit of the insulating plug. Two attempts were made at 30° and two at 75° before the final runs, which were carried through successfully with a single set-up. The experimental points lay with great

smoothness, but there was a consistent difference between the increasing and decreasing runs simply described as due to a continual creep of zero toward high values during the application and release of pressure. The effect was much larger at 75° than at 30°, where it was barely perceptible. The maximum zero creep was in copper at 75°, for which it was about 0.5 per cent of the maximum effect of pressure, that is, an increase of the original resistance by 0.00025 of itself during the run. The effect was thus always small, and there is no more reason to be concerned about it than about the seasoning effects which have been found so many times at lower pressures, even if the present effect is somewhat larger than formerly. The mean of results with increasing and decreasing pressure was taken.

The results are given in Table I. These present values may be checked against the results obtained on the same specimens 20 years ago.<sup>10</sup> At 30° and 10,000 kg/cm<sup>2</sup> the former values for  $-\Delta R/R_0$  for copper, silver, and gold were 0.01826, 0.03386, and 0.02942 respectively against 0.01857, 0.03376, and 0.02934 found now. The differences are small, and there is no consistent difference of direction, as there would be if there were important error in the measurement of pressure. I see no reason to think that the effects may not be connected with the pressure seasoning. Notice that at low pressures the pressure coefficient of copper decreases with rising temperature, an abnormal result checking the result previously found, but that between 15,000 and 20,000 the sign reverses, becoming normal.

It is of interest to inquire whether there is any notable new trend in the results at pressures above 12,000, the previous maximum. This question may be answered by extrapolation from the low pressure values. A second degree curve may be passed through the points at 5,000 and 10,000 and the curve extrapolated to 30,000. It will be found that the value of  $-\Delta R/R_0$  given in this way is in all three cases too small, but not by a large amount. The numerical excess of the actual  $\Delta R/R_0$  over that calculated is 5.23, 1.79, and 3.74 per cent respectively for copper, silver, and gold. The difference is in such a direction that the second degree extrapolation would predict a minimum at too low a pressure. Simple linear extrapolation from 10,000 and 0 would fail by two or three times as much.

Obviously only a rough significance can be attached to this result. There is no particular virtue in the second degree curve, and in fact it was already known that the experimental results to 12,000 could not be reproduced to within quite the experimental error by a second degree curve. But roughly, one significance of the fact that extra-

Pressure kg/cm <sup>2</sup>	Copper		Silver		Gold		Iron		Lead	
	$-\Delta R/R_0$	$30^\circ$	$-\Delta R/R_0$	$30^\circ$	$75^\circ$	$-\Delta R/R_0$	$30^\circ$	$75^\circ$	$-\Delta R/R_0$	$30^\circ$
5,000	0.096	0.094	0.174	0.176	0.151	0.154	0.121	0.118	0.086	0.091
10,000	0.186	0.185	0.338	0.341	0.293	0.299	0.234	0.232	0.166	0.177
15,000	0.271	0.271	0.492	0.497	0.429	0.437	0.341	0.341	0.170	0.179
20,000	0.354	0.354	0.637	0.644	0.559	0.570	0.444	0.447	0.214	0.242
25,000	0.434	0.435	0.774	0.784	0.684	0.698	0.542	0.546	0.261	0.263
30,000	0.513	0.514	0.916	0.916	0.806	0.724	0.637	0.646	0.295	0.298

pulation over a pressure range of three fold does not fall by more than a few per cent is that the manganin gauge pressure is probably not in error by any large amount.

With a relation so nearly linear as that found, it would be profitless to speculate about the existence of a pressure of minimum resistance.

*Iron.* The measurement of iron was undertaken in much the same spirit as that of copper, silver, and gold, namely because the effect of pressure up to 12,000 does not depart much from linearity, so that some presumptive evidence can be obtained as to the accuracy of the manganin gauge. The same sample of iron was used as had been previously measured up to 7,000 in the gas apparatus at liquid air temperature,<sup>11</sup> and also in my work of 1916. A short specimen was used, and the measurements were made with the potentiometer, as were the measurements on all subsequent metals.

After one failure, successful runs were made to 30,000 at 30° and 75° with a single set-up. Again the points lay very smoothly with a slight zero creep in the same direction as before, the maximum creep at 75° being less than 1 per cent of the pressure effect or 0.0005 of the initial resistance.

The results are given in Table I. Second degree extrapolation from 5,000 and 10,000 gives at 30,000 a  $\Delta R/R_o$  too small numerically by 6.5 per cent on the measured value.

*Lead.* The specimen was the same as that measured previously to 7,000 in the gas apparatus at liquid air temperature.<sup>11</sup> Measurements were made successfully with a single set-up to 30,000 at 30° and 75°. Zero creep or other seasoning effects were now almost imperceptibly small, doubtless because of the mechanical softness, and the greater magnitude of the change of resistance.

The experimental results are given in Table I. At 30° and 10,000 the present value of  $\Delta R/R_o$  is -0.1262 against -0.1206 found formerly. Second degree extrapolation at 30° from 5,000 and 10,000 now gives  $\Delta R/R_o = -0.3726$  against -0.2959 observed. The discrepancy is in the opposite direction than for the four previous metals. The second degree relation is thus not nearly as good an approximation as for the other metals in which the absolute magnitude of the pressure effect is less. If  $\log(-\Delta R/R_o)$  is plotted against pressure a curve is obtained which does not depart greatly from linearity, being gently convex toward the pressure axis. If now a second degree curve is passed through the 15,000 and the 30,000 points of this logarithmic curve, extrapolation indicates a minimum in resistance at 82,000 kg/cm<sup>2</sup>. The only conclusion is that if there is a minimum it is probably well beyond present experimental possibilities.

*Lithium* The material was from Kahlbaum. It was extruded into a wire about 0.030 inches in diameter, and connections made with spring clips. Successful runs were made to 30,000 at 30° and 75° with a single set-up. The maximum difference between points with increasing and decreasing pressure was at 75°, where it was 1 per cent of the maximum pressure effect. The effect was not a zero creep, but rather a permanent alteration of resistance after application of the maximum pressure, this might well be due to mechanical distortion in this relatively soft metal.

The numerical results are given in Table II. The resistance of

TABLE II  
RESISTANCE OF LITHIUM

Pressure kg/cm <sup>2</sup>	Resistance		Pressure kg/cm <sup>2</sup>	Resistance	
	$R/R(0, 30^\circ)$ 30°	$R/R(0, 75^\circ)$ 75°		$R/R(0, 30^\circ)$ 30°	$R/R(0, 75^\circ)$ 75°
2,500	1.0175	1.0172	17,500	1.1318	1.1449
5,000	1.0354	1.0351	20,000	1.1524	1.1553
7,500	1.0539	1.0537	22,500	1.1735	1.1770
10,000	1.0727	1.0730	25,000	1.1949	1.1992
12,500	1.0920	1.0928	27,500	1.2169	1.2221
15,000	1.1117	1.1131	30,000	1.2394	1.2453

Lithium has been previously measured to 12,000. The resistance increases under pressure and at an accelerated rate, the curve of resistance against pressure being convex toward the pressure axis. Although this is the direction of curvature for all metals with positive pressure coefficient, with the exception of antimony, it was of particular interest to find whether the upward curvature would continue, in view of a suggestion which has been made theoretically that the resistance might pass through a maximum at high enough pressures. Inspection of the Table shows that the upward curvature does indeed continue up to 30,000. The first differences are nearly linear in the pressure, which means a second degree relation between resistance and pressure.

The increment of resistance found formerly at 10,000 at 30° was 7.57 per cent against 7.27 found now. The direction of the difference would indicate higher purity in the present sample. Another indication in the same direction is that the temperature coefficient at atmospheric pressure found now is very materially higher than the previous value. However, I do not give the figure for this coefficient,

since the possibility of chemical action was not ruled out by making a return check reading at  $30^\circ$

*Sodium* The material was from the same source as that used in my previous measurements of volume to 20,000<sup>1</sup>. It was extruded into wire about 1.3 mm in diameter, and connections made with spring clips of fine wire, as with lithium. A run was made at  $30^\circ$  to 30,000 and back to 12,000, when one of the leads open circuited. Since the primary question with regard to this substance, namely whether there was a minimum in the resistance, was answered by these measurements, I did not attempt to complete the measurements by setting up the apparatus again, but as already explained, preferred to use the time in measurements on other substances.

The results are shown in Table III, in which are shown also my

TABLE III  
RESISTANCE OF SODIUM

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$		Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	
	Present Values	Former Values		Present Values	Former Values
2,500	8529	8515	17,500	5049	5021
5,000	7537	7480	20,000	4813	
7,500	6762	6731	22,500	4619	
10,000	6171	6141	25,000	4456	
12,500	5708	5671	27,500	4324	
15,000	5341	5308	30,000	4223	

previous results for comparison.<sup>12</sup> The agreement, particularly at the high pressures, is satisfactory. The previous measurements reached a maximum of 18,000, from these measurements I extrapolated the curve of first differences to a probable minimum at 28,000. This pressure was exceeded in the present measurements, but the minimum does not occur below 30,000, which simply means that the curve of first differences is not as nearly linear above 18,000 as I drew it. In fact the curvature is so great that extrapolation now appears more hazardous than before, it seems to me now that the most probable location of the minimum is in the neighborhood of 40,000. But it must be admitted that if I had only the data for sodium without those of the other alkali metals also, I would now have much less assurance of even the existence of a minimum than I had when I had only the measurements up to 18,000.

*Potassium* The material was from Kahlbaum, it was extruded to bare wire and mounted for the resistance measurements in the same

way as lithium and sodium. At 30° a successful run was made to 30,000 and back. At 75°, the highest reading was made at 25,000, on trying for the maximum pressure the lower reinforcing ring on the outside of the pressure cylinder ruptured, the only time a similar accident has occurred in all this work. I did not attempt to complete the measurements with another set-up. At 30° there was some divergence between the runs with increasing and decreasing pressure, doubtless because of mechanical distortion of this very soft metal. The readings with decreasing pressure at 30° were taken as most probably accurate. Neither was any attempt made to get very accurate values at the lowest pressures, where the change of resistance is so large that any extrapolation to zero would have been inaccurate. Instead, the low pressure values were so chosen as to agree with my former values up to 5,000. At 75° the values under 5,000 were inaccurate. Also because of the impossibility of checking the zero at 75° there may have been an error at the lower pressure due to chemical action such that all the tabulated resistances may be too high with regard to those at 30° by a constant factor.

The most interesting question presented for the measurements on potassium is whether the minimum of resistance expected on the basis of my previous measurements<sup>12</sup> to 18,000 actually occurs. My former extrapolated value for the pressure of the expected minimum was 23,500. Table IV shows at once that the minimum does occur

TABLE IV  
RESISTANCE OF POTASSIUM

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$		Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	
	30°	75°		30°	75°
0	1,000		22,000	1,760	
2,500	664		23,000	1,740	216
5,000	491	615	24,000	1,726	
7,500	378	467	25,000	1,719	216
10,000	303	372	26,000	1,721	
12,500	253	310	27,000	1,729	
15,000	219	269	28,000	1,740	
17,500	197	242	29,000	1,756	
20,000	1821	224	30,000	1,778	
21,000	1788				

In the lower part of the Table are shown the results in the neighborhood of the minimum at 30° to one more significant figure than in the rest of the Table. The measurements were accurate enough to give

the *relative resistance* to four figures, the absolute resistances, however, are not accurate to four significant figures. At 30° the minimum appears to be at 25,400, about 2,000 higher than the previously extrapolated value. The discrepancy is in the same direction as found already for sodium, but by not so large a factor, as would be expected because the extrapolation is not over so wide a range. At 75°, the minimum is perceptibly lower, at about 24,000. This shift in pressure of the minimum with temperature means that in the neighborhood of this pressure there is a notable increase in temperature coefficient of resistance, for pressures up to this point the variation of temperature coefficient with pressure is not large, as is also the case with most other metals.

*Rubidium*.—The material was from the same lot as that used in my previous measurements.<sup>12</sup> This metal is so soft that the difficulties of using it in the form of wire seemed prohibitive; it was therefore enclosed in a glass envelope. The envelope was in the form of a U, the upper ends of the legs of the U, in which were sealed the platinum leads, being about 3 mm inside diameter, and the lower part of the legs, containing the part subjected to measurement, about 2 mm in diameter and 2 cm long. The proportions were made short and thick in order to minimize the restraining effect of the glass. If the U is long and slender the differential compression of the glass and rubidium demands so much relative motion that there is much distortion, and the column may even be ruptured. The U was filled in vacuum. The filling apparatus was provided with four successive chambers, and the rubidium was driven from one chamber to the next by distillation at the lowest feasible temperature, each chamber being sealed off in turn as it was emptied of its charge. In this way the impurity of oxide, which dissolves in the metal, can be removed. Previous work had shown no appreciable metallic impurities. The walls of the U were made as thin as convenient in the hope that they would completely rupture under pressure, leaving the metallic rubidium unconstrained. This was not accomplished with complete success however, the glass ruptured, but it ruptured into slender longitudinal shivers, so that the distance between the potential terminals was still set by the glass and its compressibility, instead of by the rubidium. Since the compressibility of rubidium is greater than that of glass, the distance between the potential terminals is greater under pressure than it would be if the metal were free, and, to compensate, the cross section must be less. Both effects work together in making the resistance under pressure too high.

Two attempts were made with this metal. The second yielded measurements at 30° up to 30,000, back to 22,000, up to 26,200, and back to 20,700, before there was open circuit. I made no further attempt to complete the measurements at 75°. The results on the initial increase of pressure are summarized in Table V. These values

TABLE V  
RESISTANCE OF RUBIDIUM

Pressure kg/cm <sup>2</sup>	Relative Resistance at 30°		Pressure kg/cm <sup>2</sup>	Relative Resistance at 30°	
	Present Values	Former Values		Present Values	Former Values
0	1 000	1 000	17,500	358	310
2,500	615	656	20,000	376	314
5,000	471	504	22,500	404	
7,500	407	416	25,000	447	
10,000	371	364	27,500	504	
12,500	354	333	30,000	576	
15,000	350	316			

are not particularly good for the absolute resistance, because of unknown effects connected with the constraint exerted by the glass and the inevitable distortion of a metal as soft as this, which resulted in permanent alterations of resistance after application of pressure, so that successive excursions did not give coincident readings.

Rubidium is already known from previous work to have a minimum in its resistance. The principal interest of these measurements over an extended range did not therefore lie in establishing the existence of the minimum, but rather in determining whether there is a polymorphic transition between 20,000 and 30,000. One might be expected because of analogy with caesium, which I had already found to have such a transition. Very careful exploration was made for a discontinuity in the resistance of rubidium, which would indicate a transition, taking readings much closer together than usual, but no effect was found. I do not believe that a discontinuity in resistance of more than 0.0003 of the initial resistance would have escaped detection. We shall presently see that the discontinuity in resistance at the transition of caesium is 0.04, so that it is highly improbable that rubidium has a transition in this range. This negative result was confirmed by measurements of the volume in the other apparatus.

The pressure of the minimum of resistance given in the table above is 15,000, against the value 17,000 found before. Because the previous measurements were made with bare wire, there is no doubt that

they are to be preferred. The former values of  $\Delta R/R_0$  are also given in the table for comparison. The present values lie too high, as was to be expected because of the character of the constraint. It was a surprise that the divergence was not greater, it was not nearly as great as would be demanded by the difference of compressibility, assuming the glass to be perfectly effective in exerting constraint.

Besides the question of minimum and transition point, it was also of interest to find whether the upward curvature in resistance continues over this new pressure range. A plot of first differences against pressure shows that they get larger numerically at an accelerated rate at the upper end of the pressure range, so that the upward curvature increases. However, the deviation from linearity between first differences and pressure is only slight, so that this conclusion has to be taken with reserve because of the unknown effect of constraint by the glass.

TABLE VI  
RESISTANCE OF CAESIUM

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$		Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	
	$30^\circ$	$75^\circ$		$30^\circ$	$75^\circ$
0	1 000		20,000	1 917	2 360
2,500	807		22,070	{ 2 203	
				{ 2 439	
5,000	812	1 046	22,420		{ 2 932
7,500	884	1 117	22,500	2 492	{ 3 056
10,000	1 005	1 200	25,000	2 836	3 491
12,500	1 160	1 450	27,500	3 230	3 972
15,000	1 376	1 685	30,000		4 509
17,500	1 624	1 984			

*Cesium*. The material was freshly obtained from Mackay, provided sealed in glass tubes, not under oil, but clean metal. A number of attempts were made before a successful pressure run was made. Like rubidium, it was impossible to work with the bare metal, but it had to be sealed in glass. The final method was the same as that finally adopted for rubidium in the light of experience with caesium. With the final filling runs were made at both  $30^\circ$  and  $75^\circ$  up to about 29,000, and then again at  $30^\circ$ . Cesium has a minimum in resistance at low pressures, the feature to be particularly studied in these measurements was the effect of passing through the transition near 22,000 which had already been established with the 50,000 apparatus. The

readings were surprisingly regular, and were almost exactly reproducible with increasing and decreasing pressure. This was not to be expected in the light of the results with rubidium, and in view of the

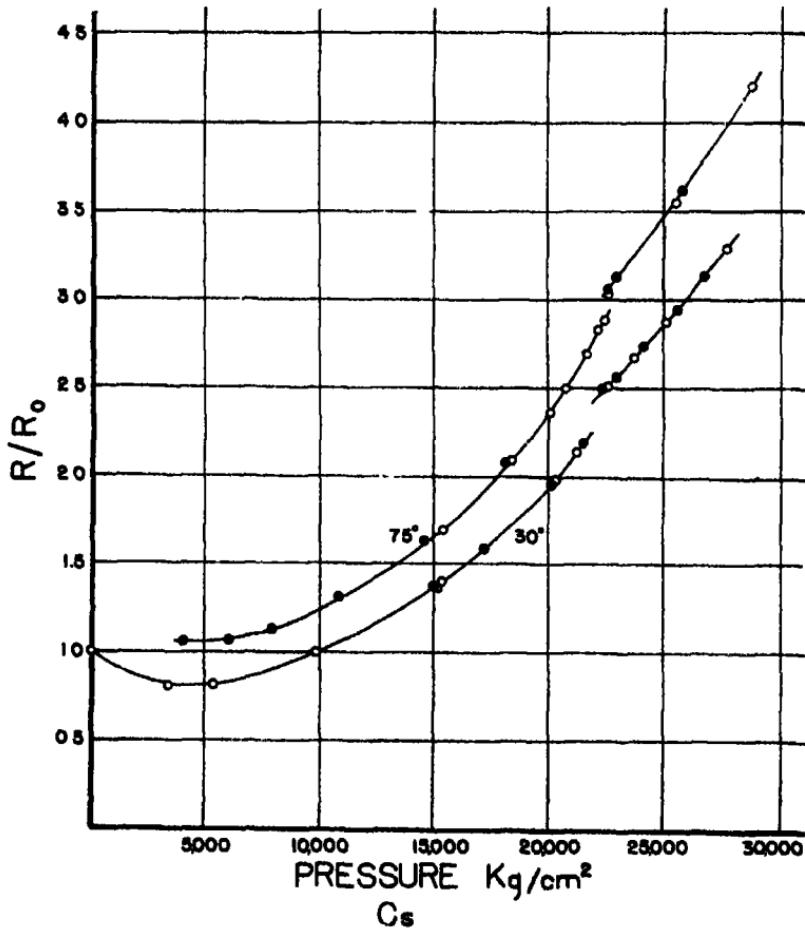


FIGURE 5 The relative resistance of caesium as a function of pressure at 30° and 75°. Open circles, increasing pressure, filled circles, decreasing pressure.

constraint exerted by the glass. One arm of the glass  $U$  did not even crack under pressure, and the other received only a single longitudinal crack for its entire length. The results are shown in Table VI and also in Figure 5. There is an upward jump in resistance at the transi-

tion point, in spite of the decrease of volume. There is only one other known example of this sort of behavior, Bismuth II to Bismuth III, in which the resistance change at a transition point runs contrary to

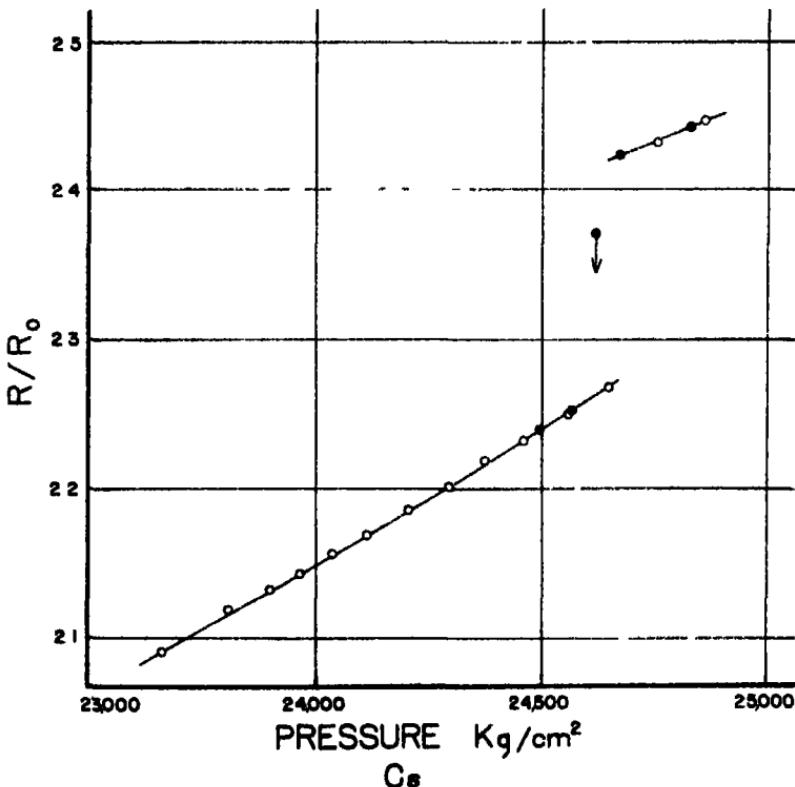


FIGURE 6 Relative resistance of caesium on a much enlarged scale in the neighborhood of the phase change. Open circles, increasing pressure, filled circles, decreasing pressure. The arrow on one point indicates that equilibrium was not reached, but resistance was decreasing in the direction indicated.

the direction of volume change. Furthermore, the resistance of the new modification also increases under pressure, and with upward curvature. There is, however, a very marked drop in the magnitude of the positive pressure coefficient on passing the transition point.

The second run at 30° was especially devoted to getting the transition point as accurately as possible and to finding how sharp the

transition is. Readings were made at intervals of only  $100 \text{ kg/cm}^2$  up and down through the transition. The apparatus has to be handled carefully to give such small pressure steps, in making the manipulations advantage was taken of the fact that the resistance of caesium is much more sensitive to pressure changes under these conditions than is the manganin gauge. In Figure 6 are plotted the points obtained in this way. The sharpness of the transition was a great surprise, there being no appreciable transgression of the transition point in either direction, a very unusual effect, particularly with such a small amount of material. The transition was shut between two pressures from above and below differing by only  $2.3 \text{ kg/cm}^2$ . This would seem to suggest that the mechanism of transition is something unusual. At  $75^\circ$  I did not make such elaborate attempts to determine the transition accurately, but within the corresponding greater uncertainty no lag phenomena were found, the transition was actually enclosed between limits differing by  $400 \text{ kg/cm}^2$ . The transition pressure increases somewhat with rising temperature, being 22,070 at  $30^\circ$  and 22,420 at  $75^\circ$ . The discontinuity of resistance at the transition is a strong temperature function, being 10.6 per cent at  $30^\circ$  and only 4.2 per cent at  $75^\circ$ . In fact the two curves suggest that at still higher temperatures the direction of discontinuity might reverse. The direction of change of resistance at the transition may therefore be more or less accidental.

The temperature coefficient of resistance of II above the transition is very nearly the same as that of I below the transition. It may be at once concluded from the table that the mean coefficient  $0^\circ\text{--}100^\circ$ , assuming a linear relation between resistance and temperature, of I at 15,000 and 20,000 is 0.00553 and 0.00581 respectively, whereas that of II at 22,500 and 27,500 is 0.00570 and 0.00556 respectively. The coefficient of I appears to decrease markedly with rising pressure at the lower pressures, being 0.00709 at 5,000. All these values are somewhat uncertain because of the constraining effect of the glass.

*Calcium* The material was extruded wire obtained from the General Electric Co. some 15 years ago. It has been kept since in a bottle with cork stopper impregnated with paraffin. Protection from oxidation had not been perfect, perhaps one third of the diameter of the wire being oxidized away. The oxide layer was rubbed off with emery paper, leaving a shiny metallic wire, flexible enough to permit a single sharp bend with care. Connections were made with spring clips in the conventional way. Two runs were successfully made to 30,000 at  $30^\circ$  and  $75^\circ$  with a single set-up and without accident. There

was some seasoning effect at 30°, the final zero being displaced by 2.8 per cent of the maximum pressure effect, or about 1.25 per cent on the total resistance. At 75° there was no appreciable difference between increasing and decreasing measurements. This also indicates freedom from chemical action, so that a satisfactory value of the temperature coefficient should be obtainable from the difference of zero readings, in spite of the fact that a return check reading at 30° was not made. It would appear that whatever the nature of the seasoning effect, it had been completed by the first application of 30,000. For this reason the measurements at 30° used in the final calculations were those obtained with decreasing pressure. The points were always regular, the maximum departure of any single point from a smooth curve being at 75°, 0.07 per cent of the maximum pressure effect.

TABLE VII  
RESISTANCE OF CALCIUM AND STRONTIUM

Pressure kg/cm <sup>2</sup>	Calcium		Strontium	
	$R/R(0, 30^\circ)$	$30^\circ$	$R/R(0, 30^\circ)$	$30^\circ$
0	1.0000	1.1688	1.0000	1.0974
2,500	1.0237	1.1922	1.1141	1.2140
5,000	1.0400	1.2187	1.2448	1.3451
7,500	1.0764	1.2485	1.3922	1.4908
10,000	1.1069	1.2816	1.5562	1.6510
12,500	1.1407	1.3178	1.7364	1.8258
15,000	1.1772	1.3571	1.9333	2.0153
17,500	1.2164	1.3998	2.1467	2.2105
20,000	1.2582	1.4460	2.3767	2.4377
22,500	1.3025	1.4959	2.6273	2.6703
25,000	1.3491	1.5485	2.8905	2.9187
27,500	1.3983	1.6033	3.1695	3.1805
30,000	1.4500	1.6603	3.4665	3.4585

The smoothed results are given in Table VII. The curves are smooth, with no particular feature. First differences increase nearly linearly with pressure over the entire range at both temperatures, so that the resistance can be represented as a function of pressure very nearly by an expression in the second degree. The temperature coefficient of resistance depends markedly on pressure, being 0.00417, 0.00376, and 0.00357 at 0, 15,000 and 30,000 respectively.

The effect of pressure on the resistance of calcium has been previously measured.<sup>14</sup> The former values for the relative increase of

resistance at 30° at 5,000 and 10,000 were 0.0548 and 0.1199 respectively against the present values 0.0490 and 0.1069. The new values are thus considerably lower. This means greater purity in the present sample. Greater purity is also vouched for by the higher value of the temperature coefficient at atmospheric pressure, 0.00417 against the former value 0.00333. The new value is higher than the highest value reported in the literature,<sup>16</sup> 0.0038, whereas the former value was distinctly low. The much greater mechanical softness of the new sample compared with the old is also an indication in the same direction.

*Strontium*.—The material was obtained from Eimer and Amend a number of years ago, and has been kept since under oil in a glass stoppered bottle. There has been appreciable surface chemical action. The surface was scraped to the pure metal, and the specimen formed into wire about 0.030 inches diameter by hot extrusion. Connections were made with spring clips as usual.

Three unsuccessful attempts, vitiated by leak or trouble with the insulating plug, were made before the fourth and successful attempt. Two runs were then made with a single set-up to 30,000 at 30° and 75°. Open circuit developed on the final reading at 75°, so that the check readings could not be made for temperature coefficient. There was no consistent difference between the readings with increasing and decreasing pressure, which, however, were not as smooth as usual. The maximum deviation of any reading from a smooth curve was at 30° at 27,000, the point lying high by 1 per cent of the total resistance at that point. Few of the other departures from smoothness were as much as one fifth of this.

The smoothed results for proportional resistance are given in Table VII. The resistance increases under pressure by a larger factor than for any other substance yet examined, the increase at 30,000 being by a factor of approximately 3.5. The curvature continues upward over the entire range, first differences against pressure rising linearly, so that a second degree equation in the pressure very approximately represents the results. The rate of increase is somewhat less at the higher temperature.

This specimen of strontium is probably of comparatively low purity, as shown by the low temperature coefficient, 0.00240, against my former value 0.00383. Unfortunately my former very pure strontium was exhausted. It appears from the table that the temperature coefficient reverses sign at the very upper end of the pressure range. This is highly unusual, and may well be an effect of the impurities.

At any rate, these data should not be used for a temperature coefficient, it has been my experience that the pressure coefficient is much less sensitive to impurity. There is nevertheless an anomaly in the pressure coefficient, my former value for the relative resistance at 30° and 10,000 was 1.66, against 1.55 now found. The lower value is usually associated with higher purity, this cannot be the case here.

*Barium* My old supply of barium was exhausted, this was new stock, obtained from Mackay. The purity was not as high as that of the former, as suggested by the low value of the temperature coefficient of resistance, which was of the order of 0.004 against 0.0065 before. The metal was formed into wire of diameter 0.0030 inch by hot extrusion, and connections were made with spring clips as usual. Instrumental difficulties accumulated capriciously in an unusual degree in working with this material, and six different set-ups were made in all. The difficulties were almost always failure of insulation of the leads. There was also appreciable chemical action during a run, so that the readings with decreasing pressure did not follow those with increasing pressure, but the resistances with decreasing pressure lay high. A mean of the increasing and decreasing readings was taken as the best, but there were irregularities which would particularly affect the location of the minimum resistance, which previous measurements<sup>16</sup> had shown to be possessed by this substance. According to my custom, the measurements were made on this substance, roughly plotted to ensure against any large discrepancy, and then put away for exact calculation at a later time. After the measurements of resistance had been thus completed, the compression was measured in the 50,000 apparatus, and a small but perfectly definite transition discovered. This transition is of the ice type, running from 17,500 kg/cm<sup>2</sup> at 0° C to 15,300 at 200°, with an average volume change of 0.00155 cm<sup>3</sup>/gm, or 0.56 per cent on the volume. On returning to the measurements of resistance it then appeared that there was a small break in the resistance at 75° on decreasing pressure, at a little less than 15,000. The resistance readings at 30° and with increasing pressure at 75° were at too wide intervals and were too irregular to show any discontinuity. The apparatus was accordingly set up again for repetition of the resistance measurements. Again there were difficulties with the insulation at 30°, but a new set-up for 75° gave perfectly good results. Regular readings at short intervals were made in the range from 14,000 to 21,000, and breaks in the resistance found. The break occurred at 19,200 with increasing pressure and 14,900

with decreasing. The break with decreasing pressure thus occurs at practically the same place as had been found before. The mean pressure of the breaks, 17,050, is to be compared with 16,700, the equilibrium pressure at 75° found with the volume apparatus. The agreement is as close as could be expected in view of the width of the region of indifference.

The discontinuity in resistance is a drop with increasing pressure, thus being in the normal direction, that is, following the change of volume. The break is somewhat greater with decreasing pressure than with increasing, which means that the positive pressure coefficient of resistance of the high pressure modification is slightly greater than that of the low pressure modification. The discontinuity with decreasing pressure was very nearly the same on repetition as had been found at first. This suggests that the volume change during the transition repeated itself, with no geometrical distortion. This again suggests that the high pressure modification as well as the low pressure modification has some simple cubic structure. The average break in resistance was 0.35 per cent of the initial resistance.

The transition phenomena of barium thus are quite unlike the transition phenomena of caesium in the sluggishness and width of indifference of the transition. It is probable therefore that the mechanism of the transition, that is, nucleus formation and the geometry of the change of position from one lattice to another, is distinctly different in the two cases. However, it is to be remembered that the effective temperature in barium is very much lower than that of caesium because barium is so much further from its melting point. Because of the error due to the width of the region of indifference I did not take the trouble to try for accurate measurements of the transition at 30°.

Caesium and barium are alike in some aspects of the behavior of resistance in passing through the transition. Usually resistance is very sensitive to changes of volume, but here the resistance is little affected, the transition occurring with small discontinuity in resistance and with very little change in the direction of the curve.

The large scale irregularities were great enough to mark the effect of the transition, so that in smoothing the results one could smooth right over the transition, ignoring its existence. The resistances smoothed in this way are given in Table VIII. In broad outline the behavior is the same as for all other metals: upward curvature increasing with pressure. Compared with previous results, the variation with pressure is not quite so great as before, and the minima are

located at somewhat higher pressures. The former values for relative resistance at 30° at 5,000 and 10,000 were 0.968 and 0.965 against 0.971 and 0.970 found now. The minima were formerly found to occur at 9,100 and 9,600 at 30° and 75° respectively, against 7,750 and 9,500 found now. The former results are doubtless to be preferred because of the greater purity of the former material.

TABLE VIII  
RESISTANCE OF BARIUM

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$		Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	
	30°	75°		30°	75°
0	1.000	1.156	17,500	0.995	1.123
2,500	0.982	1.130	20,000	1.008	1.140
5,000	0.971	1.114	22,500	1.025	1.161
7,500	0.967	1.107	25,000	1.044	1.181
10,000	0.970	1.106	27,500	1.066	1.211
12,500	0.976	1.108	30,000	1.092	1.241
15,000	0.984	1.113			

*Mercury.* The particular object of the run was to get measurements on the resistance of solid mercury over a more extended range than the 12,000 kg/cm<sup>2</sup> investigated hitherto,<sup>17</sup> and also to obtain a value for the melting pressure at a higher temperature. The mercury was ordinary distilled laboratory stock, which previous experience had shown to be amply pure enough since it gives sharp freezing points. It was mounted in a very thin glass *U*, with four platinum leads sealed in. The procedure was to first make measurements on the liquid phase at 30° with increasing pressure until the freezing pressure was reached. On completion of freezing, measurements were then made on the solid up to 30,000, and then back to a pressure sufficiently above the freezing pressure so that there was no danger of melting. Pressure was then raised to above the freezing pressure at 75° as extrapolated from previous measurements, temperature raised to 75°, readings made with increasing pressure up to 28,000, and then back in steps of 1,000 until the melting point was reached. Fortunately the final setting was made almost exactly on the melting point, permitting an accurate evaluation of the melting pressure at 75°. It was possible to be sure of this because the increase of resistance indicating melting did not begin to manifest itself until after waiting nearly ten minutes at constant pressure, which is more than the time required under normal conditions for complete attainment of temper-

ature equilibrium. The reason that melting did not take place at once was that at first on reaching this pressure the temperature was slightly depressed as a result of the decompression, and only after waiting some time did temperature creep back to the melting point. Previous experience with other materials would indicate that the maximum temperature effect of decompression is only a small fraction of a degree under these conditions, so that the melting coordinates should be fairly exact. On further release of pressure at 75° below the melting pressure the circuit opened, as was expected, because of escape of liquid mercury from the ruptured capillary, rupture doubtless having taken place on the first freezing at 30°.

All the experimental points, on both solid and liquid phases, were very regular and with no hysteresis, the departure from a smooth curve being hardly perceptible in any case. At 30°, the lowest reading on the liquid was at about 4,000 kg/cm<sup>2</sup>. The zero was calculated so as to make the change of resistance for the first 4,000 kg agree with my previous measurements.

TABLE IX  
RESISTANCE OF MERCURY

Pressure kg/cm <sup>2</sup>	Resistances		Resistances		
	Liquid $R/R_0$	30°	Pressure kg/cm <sup>2</sup>	30°	75°
0	1 0000		13,590	1 000	
4,000	9076		15,000	967	
6,000	8635		17,500	917	
8,000	826		20,000	871	
10,000	792		22,500	830	987
12,000	761		25,000	793	940
13,590	738		27,500	760	897
			30,000	730	857

The numerical results are given in Table IX. The resistances of the solid are given in terms of the resistance at the freezing point at 30°. This freezing pressure, 13,590 kg/cm<sup>2</sup>, was obtained by an extrapolation from 12,000 of my previous measurements. The values for the liquid are relative to the resistance of the liquid at atmospheric pressure at 30°, the zero having been determined, as already explained, so as to make the change of resistance at 4,000 agree with the former value. In all cases, the resistances tabulated are the measured resistances. The specific resistance differs from this by a factor depending

on the change of dimensions. For the liquid phase, the change of dimensions is that of the glass capillary. The compressibility of the glass was not known. If an average value 0.0000024 (cubic compressibility per kg/cm<sup>3</sup>) is assumed, it will be found, for example, that the specific resistance of the liquid at 10,000 is 0.7858 of its initial value, against 0.7863 in my previous measurements. The agreement is as close as could be expected in view of the unknown difference between the compressibility of the glass capillaries in the two experiments. The measured resistances of the solid, on the other hand, are probably not at all affected by the glass, which was thin and had ruptured. Absence of constraint by the glass was also indicated by the complete absence of any pressure hysteresis. The measurements on the solid are therefore strictly comparable with the measurements on other solid substances in this paper, namely, they are measurements of the resistance between terminals attached to the specimen. The correction factor to convert to specific resistance is the linear compressibility of the solid, this is not known for solid mercury under these conditions.

On freezing at 30° the resistance dropped by a factor of 2.99. If it can be assumed that freezing took place without rupturing the glass capillary, some information can be extracted from the value of this ratio. This is somewhat smaller than the rough average found in my previous work. The crystal structure of mercury is tetragonal, and the ratio of the resistances along the two axes at atmospheric pressure is 0.756,<sup>18</sup> the resistance along the tetragonal axis being, abnormally, the lower. It is not unlikely that the solid measured above was mostly a single crystal, since freezing took place very slowly (it could be followed by following the change of resistance). The low value of the ratio, values obtained under ordinary conditions being in the neighborhood of 4, would therefore mean that the predominant orientation was with the tetragonal axis perpendicular to the axis of the specimen. The pressure coefficient measured above may, therefore, be the pressure coefficient for this predominant direction.

The pressure coefficient of resistance of the solid is high, being in the neighborhood of -0.00002 at the freezing point at 30°. This may be compared with -0.000014 for lead. At the freezing point at 30° the rate of change with pressure of the resistance in ohms of a specimen with fixed dimensions is somewhat greater in the solid than the liquid phase. This means that the coefficient of the solid is more than three times as great as that of the liquid at the freezing point.

The temperature coefficient of the solid may be computed from the

table. It is somewhat greater than  $1/\tau$ , as would be expected for a soft metal with a low melting point, and decreases somewhat with rising pressure, being 0.00467 at 22,500 kg and 0.00426 at 30,000.

The freezing pressure at  $75^\circ$  was 22,570 kg/cm<sup>2</sup>. Previous measurements up to  $20^\circ$  had shown the melting curve to be very nearly linear in pressure, the first differences increasing slightly. If it be assumed that the first difference increases linearly, being 1,980 kg/cm<sup>2</sup> per  $10^\circ$  at  $20^\circ$  and 2,010 at  $80^\circ$ , it will be found that the extrapolated melting pressure at  $75^\circ$  is 22,595 against 22,570 measured above. Linear extrapolation from  $-30^\circ$  and  $+20^\circ$  gives 22,446 kg/cm<sup>2</sup> at  $75^\circ$ . The presumption is that the manganin pressure gauge is not far off. The curvature of the melting curve of mercury is among the smallest, if not the smallest, of any measured.

**Zinc** Measurements were made on two single crystal specimens, the identical specimens which I had previously used up to 7,000 at liquid air temperature.<sup>19</sup>

TABLE X  
RESISTANCE OF SINGLE CRYSTAL ZINC

Pressure kg/cm <sup>2</sup>	Axis 87° to length		Axis 17° to length	
	$R/R(0, 30^\circ)$	$30^\circ$	$R/R(0, 30^\circ)$	$75^\circ$
0	1.0000	1.1627	1.0000	1.1650
2,500	0.9868	1.1488	0.9756	1.1352
5,000	0.9744	1.1355	0.9525	1.1062
7,500	0.9628	1.1228	0.9300	1.0809
10,000	0.9518	1.1107	0.9081	1.0562
12,500	0.9410	1.0991	0.8882	1.0325
15,000	0.9321	1.0880	0.8686	1.0103
17,500	0.9233	1.0776	0.8500	0.9880
20,000	0.9150	1.0677	0.8321	0.9687
22,500	0.9072	1.0582	0.8153	0.9495
25,000	0.8998	1.0498	0.7990	0.9310
27,500	0.8926	1.0420	0.7835	0.9129
30,000	0.8855		0.7687	0.8959

(1) Axis inclined at  $87^\circ$  to the length. At  $30^\circ$  a successful run was made up to 30,000 and back, at  $75^\circ$  with the same set-up readings were obtained only with increasing pressure up to 25,000; at 30,000 a permanent ground developed on one of the leads. At  $30^\circ$  there was a permanent increase of resistance of unexplained origin between 25,000 and 30,000, amounting to 1.3 per cent of the initial resistance. The decreasing curve ran parallel to the increasing curve. The decreasing

curve at  $30^\circ$  and of course the increasing curve at  $75^\circ$  were used to give the final results. All points at both temperatures lay on smooth curves without perceptible deviation. There is no indication of a discontinuity, and therefore of a transition.

The results are given in Table X. The first differences are convex toward the pressure axis, the curvature of the line of first differences becoming greater at the high pressure end of the line. The data give no basis for an estimate of a hypothetical pressure at which there might be a minimum resistance. The temperature coefficient of resistance is nearly constant over the entire pressure range, increasing very slightly at the higher pressures.

Previous measurements on a specimen with axis oriented at  $90^\circ$  to the length give for the proportional change of resistance at  $30^\circ$  and 10,000 0 0467, against 0 0482 above.

(2) Axis inclined at  $17^\circ$  to the length. Successful runs were made with a single set-up at both  $30^\circ$  and  $75^\circ$  up to 30,000 and back. At  $75^\circ$ , two points lay off a smooth curve by 0 7 per cent of the maximum effect, otherwise there were no important deviations.

The results are given in Table X. Comparison with previous results is not as simple as for the other orientation, and I have not attempted it. The first differences drop very nearly linearly with pressure, but with slight convexity toward the pressure axis. Any possible minimum of resistance is too remote for profitable speculation, particularly since shearing measurements make it probable that there is a polymorphic transition below 50,000. Again the temperature coefficient is very nearly independent of pressure.

The pressure coefficient is higher in the  $17^\circ$  orientation than in the other by an amount considerably higher than the difference of specific resistance in the two directions, so that as a consequence the ratio of specific resistances at first approaches equality as pressure increases. In fact, the variation of pressure coefficient with direction is so great that at 30,000 the relative resistances along the axes have reversed, the ratio at  $17^\circ$  to that at  $87^\circ$  being 0 90 against an initial ratio of 1 035. This effect is very far above any possible experimental error, it is an interesting point for the theorist.

Tin Measurements were made on two single crystal samples, the same as those previously measured to 7,000 at liquid air temperature.<sup>20</sup> (1) Axis  $17^\circ$  with the length. Successful measurements were made at  $30^\circ$  and  $75^\circ$  up to 30,000 and back with a return check reading at  $30^\circ$ . The points lay very smoothly, with no hysteresis, and no suggestion of any discontinuity that might mean a transition. The maximum

deviation of any single point from a smooth curve was 0.2 per cent of the maximum pressure effect.

The results are given in Table XI. The relation between pressure and resistance is very nearly of the second degree in the pressure, there being a slight deviation in the direction of greater curvature at the lower pressures. Previous measurements on this sample gave for the average pressure coefficient of resistance 0—10,000 at  $-79^\circ$   $-9.79 \times 10^{-6}$ , against the value  $-9.51 \times 10^{-6}$  at  $30^\circ$  found now.

TABLE XI  
RESISTANCE OF SINGLE CRYSTAL TIN

Pressure kg/cm <sup>2</sup>	Axis 17° to length		Axis 82° to length	
	$R/R(0, 30^\circ)$		$R/R(0, 30^\circ)$	
	30°	75°	30°	75°
0	1.0000	1.1734	1.0000	1.1793
5,000	0.9500	1.1139	0.9538	1.1257
10,000	0.9049	1.0508	0.9125	1.0764
15,000	0.8636	1.0111	0.8754	1.0309
20,000	0.8262	0.9671	0.8418	0.9905
25,000	0.7924	0.9274	0.8102	0.9533
30,000	0.7617	0.8905	0.7815	0.9191

The temperature coefficient is again nearly independent of pressure (2) Axis oriented at  $82^\circ$  to the length. A first attempt with this sample gave results only to 25,000 at  $30^\circ$ , beyond which there was an open circuit. A second set-up gave two complete runs at  $30^\circ$  and  $75^\circ$  up to 30,000 and back. The values obtained with the second set-up were those finally used. The first set-up gave at its maximum pressure a value agreeing exactly with that of the second, with a maximum discrepancy at intermediate pressures of 0.5 per cent of the maximum pressure effect. The maximum deviation from a smooth curve of any single reading of the second set-up was 0.2 per cent of the maximum pressure effect.

The results are shown in Table XI. Again the relation between pressure and resistance is nearly of the second degree, but with a deviation in the direction of greater curvature at the lower pressures which is somewhat greater than with the other orientation. The temperature coefficient of resistance is also nearly independent of pressure, being 0.00442 at atmospheric pressure and 0.00434 at 30,000.

Unlike the results with zinc, the pressure coefficient of resistance in different directions is much more nearly equal than the specific resistances themselves in those directions, so that there is little change

with pressure of the ratio of resistance along the two axes. What little change there is in the direction of increasing equality of resistance at high pressure?

*Antimony.* Measurements were made on two single crystals of different orientations, the identical specimens which had been previously measured to 7,000 at liquid air temperature.<sup>21</sup>

(1) Axis 87° with the length. Two set-ups, yielding only incomplete results because of leak and insulation trouble, were first made. The third set-up yielded a complete run at 30° to 30,000 and back, but at 75° readings could be made only to 15,000, beyond this the insulation going bad. There were indications of previous trouble with the insulation, the points at 30° not lying as regularly as usual. There were two bad points, lying off the curve by 1 per cent of the total resistance, but the other points lay smoothly, and the results should be essentially correct.

TABLE XII  
RESISTANCE OF SINGLE CRYSTAL ANTIMONY

Pressure kg/cm <sup>2</sup>	Axis 41° to length		Axis 87° to length	
	$R/R(0, 30^\circ)$	$30^\circ$	$R/R(0, 30^\circ)$	$75^\circ$
0	1 0000	1 1993	1 0000	1 1975
2,500	1 0246	1 2200	1 0140	1 2035
5,000	1 0547	1 2553	1 0263	1 2072
7,500	1 0891	1 2866	1 0372	1 2091
10,000	1 1264	1 3196	1 0456	1 2091
12,500	1 1633	1 3524	1 0512	1 2087
15,000	1 1978	1 3845	1 0529	1 2017
17,500	1 2289	1 4141	1 0496	1 1927
20,000	1 2557	1 4408	1 0421	
22,500	1 2781	1 4639	1 0288	
25,000	1 2959	1 4798	1 0104	
27,500	1 3085	1 4942	9850	
30,000	1 3151	1 4996	9533	

The relative resistances are given in Table XII. The resistance at first increases with pressure, then passes through a maximum, and then drops. Antimony is the only example with a maximum resistance and with curvature concave toward the pressure axis. Unless there is a polymorphic transition, there must of course be a reversal of curvature at still higher pressures, because if this curvature were to continue the resistance would presently become negative. It is,

however, highly probable that there is a polymorphic transition<sup>22</sup> below 50,000

The effect of pressure on resistance is an unusually strong temperature function. The maximum resistance occurs at 14,500 kg/cm<sup>2</sup> at 30° and at 8,800 at 75°. The curvature at 75° is considerably greater than at 30°. This results in an abnormally great decrease of temperature coefficient with increasing pressure, the coefficient is 0.00487 at atmospheric pressure, 0.00334 at 10,000, and 0.00297 at 17,500.

(2) Axis inclined at 41° to the length. A single set-up was made with this sample, yielding at 30° a complete run to 30,000 and back, and at 75° only readings with increasing pressure up to 25,000, beyond which one of the insulating stems pinched off. The readings before the final accident were entirely regular, with barely perceptible deviation from a smooth curve.

The results are given in Table XII. The resistance initially increases with pressure with normal curvature, that is, increases at an accelerated rate, but presently in the neighborhood of 5,000 there is a point of inflection, and from here on the curve rises with concavity toward the pressure axis, and is evidently headed for a maximum like the other orientation, but at considerably higher pressure. The extrapolated pressure of the maximum is just beyond the experimental range, being 31,250 at 30° and 30,250 at 75°. The variation of maximum pressure with temperature is thus not as great as with the other orientation. The temperature coefficient again drops markedly with pressure, but not by quite as much as for the other orientation, the coefficient is 0.00491 initially, 0.00320 at 15,000, and 0.00263 at 30,000.

At atmospheric pressure the resistance of single crystal antimony is highly anomalous in that the resistance for flow across the cleavage plane is less than for flow in it. Comparison of the results above for the two orientations shows that at high pressures the difference reverses sign, so that antimony becomes normal in that at a pressure roughly in the neighborhood of 13,000 the ratio of resistance in the two directions becomes equal, and at pressures above 13,000 the ratio is normal, the discrepancy in resistance becoming accentuated at an accelerated rate as pressure increases.

*Bismuth.* Measurements have previously been made up to nearly 20,000.<sup>23</sup> Bismuth has two transitions beyond 23,000,<sup>24</sup> so that there was not much point in repeating these measurements in order merely to obtain a 3,000 kg increase of range, but there was very great interest in finding the behavior of the new modifications.

Measurements were made with a single set-up, on a single crystal sample with axis inclined at  $78^\circ$  to the length, the same sample as used in previous measurements to 7,000 at liquid air temperature. With this sample a successful run was made at  $30^\circ$  up to 29,000 and back, through the two transitions in both directions. At  $75^\circ$  readings

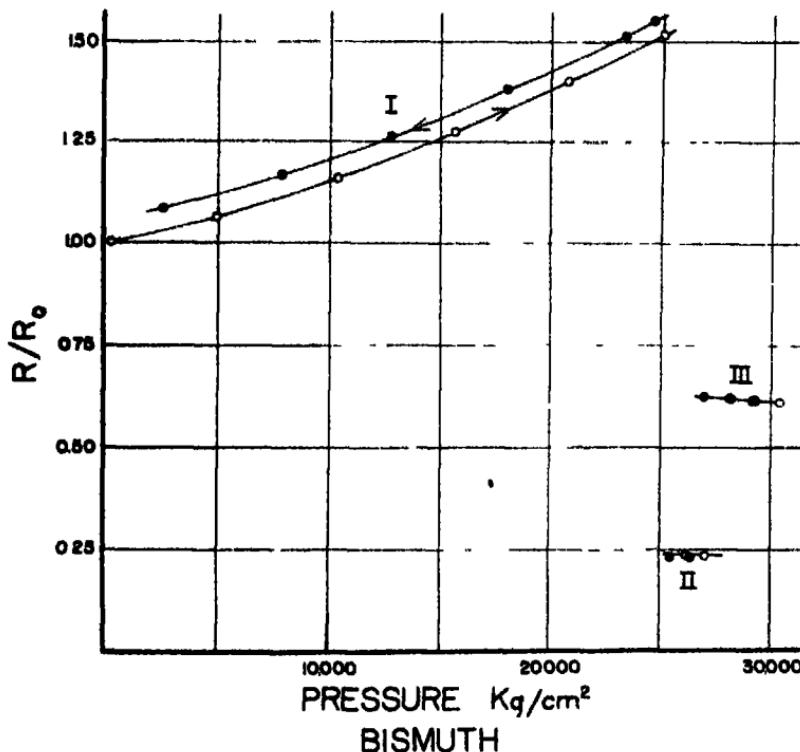


FIGURE 7 The relative resistance at  $30^\circ$  as a function of pressure of the three modifications of bismuth. Open circles, increasing pressure, filled circles, decreasing pressure.

were obtained only with increasing pressure up to 25,500, giving a reading on the third modification, beyond this there was open circuit due to pinching off of one of the stems.

The results are probably of sufficient interest to justify showing the actual experimental points, which are given in Figure 7 for  $30^\circ$ . The resistance increases with upward curvature on modification I in the way determined in previous experiments up to the transition to II.

Here there is an abrupt drop of resistance by a factor of something more than 6. The modification II is stable over only a narrow range of pressure. Measurements were obtained at two points in this range, the resistance of II drops slightly with rising pressure, as is normal. With further increase of pressure the transition to modification III is marked by an abrupt *rise* of resistance by a factor of more than 2.5. This rise of resistance is highly abnormal, it was the first example known in which the resistance on passing through a phase change (either liquid-vapor, liquid-solid, or solid-solid) goes contrary to the direction of the volume change. Since then one other example has been found, caesium, but this doubtless reverses in sign at higher temperatures. Measurements on III were made at several pressures up to 29,000 and back to the transition. Again the pressure coefficient is normal, the resistance decreasing with increasing pressure. Furthermore, the readings were reversible, the resistance under decreasing pressure retracing its course with increasing pressure. On passing the transition point from III to II, the resistance drops back by a large amount, but not to quite the former value. Failure of II to recover exactly its previous value is doubtless due to gross changes produced by the transition, probably a combination of changes of dimensions and changes in the orientations of the individual crystal grains. The latter effect would vanish if II were isotropic. There is, of course, no reason to anticipate that when the mono-crystal I transforms into II it transforms into another mono-crystal. The pressure coefficient of II with decreasing pressure is practically the same as with increasing, indicating no large change in effective orientation or else approximate isotropy of pressure coefficient of II. On further decrease of pressure, II transforms back into I, again there is the very large increase of resistance, and again the former value is not exactly regained. Release of pressure on I back to atmospheric now gives a curve with somewhat different slope from the initial slope, from which the certain conclusion can be drawn that I has not recovered its mono-crystal character. This was confirmed by subsequent examination of the specimen, it was covered with small-scale roughnesses, and the axis was no longer straight, but has several appreciable changes of direction. The over-all permanent change of dimensions was small. By comparing the initial and the final resistance it may be concluded that the transformation from the original mono-crystal to a completely haphazard aggregate is more than two thirds complete.

The run at 75° was similar as far as it went to that at 30°. Comparison between the two runs at 30° and 75° must not be pushed too far

in computing temperature coefficients etc. because of probable geometrical differences in the specimen at the two temperatures.

No extravagant attempt was made to get accurate values of the pressure of transition by taking very small pressure steps, as had been done for caesium. The size of the steps is sufficiently indicated in the figure. There was no observed over-shooting of either transition in either direction, the pressure steps were of such a size that any possible over-shooting could not possibly have been more than 1,000 kg/cm<sup>2</sup>. The transition pressures given here are the mean with increasing and decreasing pressure of the means of the extreme pressures on both sides of the transitions. The size of the pressure steps was such that the maximum error in the transition pressure should be of the order of 150 kg, assuming no over-shooting at all, the error would be somewhat larger if there was actually unobserved over-shooting within the allowable limits. At 75° the transition pressure could not be enclosed within such narrow limits, because the reverse readings were not made, except that the transition II-III should be fairly accurate because the slowness of the transition indicated that by accident the reversible transition point had been very nearly reached.

TABLE XIII

## RESISTANCE OF BISMUTH

Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$	Pressure kg/cm <sup>2</sup>	$R/R(0, 30^\circ)$
	I		
0	1.0000	22,500	1.4513
2,500	1.0295	24,700	1.5141
5,000	1.0648		II
7,500	1.1080	24,700	2.3889
10,000	1.1523	26,600	2.3555
12,500	1.2036		III
15,000	1.2592		
17,500	1.3193	26,600	6.1668
20,000	1.3833	30,000	6.0411

The relative resistances at 30° are given in Table XIII. Only the increasing points for phase I are used here, so that this part of the Table refers to the orientation with axis 78° to the length. The resistances of II and III are means with increasing and decreasing pressure, and refer to some unknown average orientation, if these phrases are not isotropic. At 75° the relative values of resistance have less significance, because they refer to an unknown initial orientation in phase I. Hence I give for 75° merely some of the data connected

with the transition. The accuracy of the original measurements is great enough to justify giving certain data more accurately than they can be taken from Table XIII. These values now follow in Table XIV. The pressure coefficients of II and III given in this table are in terms of the resistances of these phases at their respective transition points taken as unity.

TABLE XIV  
DETAILS OF RESISTANCE OF BISMUTH AT TRANSITIONS

 $30^{\circ}$ 

$$\left(\frac{R_I}{R_{II}}\right)_{24,700} = 6.339$$

$$\left(\frac{R_{III}}{R_{II}}\right)_{26,800} = 2.618$$

 $75^{\circ}$ 

$$\left(\frac{R_I}{R_{II}}\right)_{28,500} = 5.92$$

$$\left(\frac{R_{III}}{R_{II}}\right)_{25,500} = 2.32$$

Mean pressure coef II, -0.0741      Mean pressure coef II, -0.0776  
Mean pressure coef III, -0.0597

Previous Values of Transition Pressures

I-II	25,100	22,800
II-III	27,800	26,000

The former values of the transition pressures are given in the table for comparison. The discrepancy is never greater than the maximum of 1,000 set above. Measurement of pressure in the former apparatus was less sensitive than in this, so that, except for the uncertainty in the extrapolation of the manganin gauge, the new values should be preferred. Probably further work on this subject would be well worth while in connection with a more certain establishment of the pressure scale in this region. If it should prove that the transition is really much sharper than the utmost limit, 1,000 kg, allowed by the above, the transition pressure of bismuth at  $30^{\circ}$  might serve as a convenient calibration point in this region, because of the very large discontinuity in the resistance.

The temperature coefficient of II at a mean pressure in its range calculates to be 0.0047, but as already explained, this is uncertain because of the possibility of change of geometrical configuration.

*Tellurium*. Runs were made on two single crystal specimens of different orientations, the identical samples which had been previously measured up to 7,000 at liquid air temperature.<sup>25</sup>

(1) Axis oriented at  $23.5^{\circ}$  to the length. One successful run up to

30,000 was made with this at  $30^\circ$ . An attempt at  $75^\circ$  was terminated by leak. A second set-up resulted in similar failure at  $75^\circ$ . I did not pursue the matter further, so that for this orientation there are measurements only at  $30^\circ$ . The experimental points lay very regularly, with no perceptible hysteresis or deviation from a smooth curve to the number of significant figures given.

The results are shown in Table XV

TABLE XV  
RESISTANCE OF SINGLE CRYSTAL TELLURIUM

Pressure kg/cm <sup>2</sup>	23° 5 Orientation		86° Orientation
	30° C $\log R/R_0$	30° C $\log R/R_0$	75° C $\log R/R_0(30^\circ)$
0	0 000	0 000	0 689
2,500	9 720	9 616	9 304
5,000	9 278	9 261	8 965
7,500	8 973	8 934	8 670
10,000	8 698	8 640	8 410
12,500	8 453	8 378	8 182
15,000	8 239	8 145	7 980
17,500	8 054	7 937	7 803
20,000	7 890	7 754	7 647
22,500	7 743	7 592	7 510
25,000	7 614	7 448	7 390
27,500	7 501	7 321	7 285
30,000	7 401	7 210	7 194

(2) Axis oriented at  $86^\circ$  with the length. Successful measurements were made with a single set-up to 30,000 and back at both  $30^\circ$  and  $75^\circ$ . All the points lay smoothly, with almost no perceptible hysteresis or deviation from a smooth curve.

The results are given in Table XV

Compared with the previous results up to 20,000,<sup>1</sup> no striking new effect appears in the next 10,000 kg/cm<sup>2</sup>. First differences of  $\log R$  continue to decrease less rapidly than linearly with increasing pressure. Any eventual minimum in resistance is probably not reached for considerably more than another 10,000 kg/cm<sup>2</sup>, and there is a polymorphic transition before this pressure.<sup>2</sup> The effect of pressure is noticeably less for the  $23^\circ 5$  than for the  $86^\circ$  orientation. The resistance is initially less for the  $23^\circ 5$  orientation, so that as pressure increases the ratio of the resistance in different directions approaches equality. The ratio does not reverse sign, however, as it does for zinc.

At atmospheric pressure the temperature coefficient of resistance of tellurium is negative, which is characteristic of non-metallic semiconductors. This negative value becomes rapidly less numerically (for the 86° orientation) and has almost become positive at 30,000. A short extrapolation, about which there should be little doubt because of the approximate linearity of the curve, indicates that the temperature coefficient will become positive not far from 33,000. Previous results to 20,000 suggested the same behavior for the other orientation also. In respect to the temperature coefficient tellurium therefore approaches the behavior of a true metal at high pressure.

### SUMMARY

I shall not attempt any theoretical discussion of the significance of these results. It is to be remarked, however, that the theoretical physicist is rapidly finding how to make wave mechanical calculations of resistance as a function of pressure, so that speculation on the theoretical significance of the results and comparison of theory and experiment may safely be left to those more competent. A brief summary of the results will, however, probably be worth while.

The comparatively hard metals, copper, silver, gold, and iron behave about as one would expect up to 30,000 from extrapolation of the behavior to 12,000. The deviation from the extrapolated value is in such a direction that any minimum of resistance probably occurs at a higher pressure than that extrapolated from measurements up to 12,000. For the softer metals of the remainder of the paper extrapolation from values up to 12,000 only proves hardly profitable. In general, the broad features of resistance found over the lower pressure range are preserved. With one exception, the resistance of all metals when plotted against pressure shows upward curvature, whether the coefficient is positive or negative. If the metal has a positive coefficient, the curvature usually increases at higher pressures.

Among the alkali metals, the resistance of sodium was found not to pass through a minimum below 30,000, as had been expected from previous work to 18,000, but the minimum now appears to be beyond 40,000. The minimum expected for potassium is actually realized not far beyond the anticipated pressure. The minimum of rubidium formerly found is verified, the resistance continues to increase regularly over the entire range beyond the minimum, with no hint of a transition. The resistance of caesium takes a jump upward at the transition pressure, a highly unusual effect. In general the resistance of caesium is much less disturbed than might be expected by the

transition through a change of lattice. The transition is very sharp. Theoretically this perhaps might not have been anticipated, because analytically the conditions which determine the transition seem to involve a delicate balance between two tendencies, both of them strong.

The alkali earth metals, calcium and strontium, continue their smooth upward increase of resistance over the entire range. Barium, however, shows a transition, with a very small change of resistance, and very little interruption of the smooth upward increase. The transition of barium is very sluggish, totally unlike that of caesium. Barium is body centered cubic, calcium and strontium both face centered. Difference in the behavior is therefore not surprising. The series of alkali metals is body centered cubic under normal conditions, it is highly probable that the high pressure transition of caesium is from body centered to face centered. By analogy one would expect the transition of barium to be also to face centered. But the parallelism between the alkali metal and the alkali earth series is far from perfect. The situation is complicated by the small transitions of calcium and strontium known to occur beyond the range of the present work. Serious speculation should wait for detailed calculations.

The resistance of solid mercury is found to behave about as would be expected from a soft metal in its position in the periodic table. The melting curve can be extrapolated over nearly double its former range with unexpected accuracy, the curvature of the melting line is abnormally low.

Single crystal zinc at high pressures shows a reversal of relative resistance along the axes, the resistance along the axis becoming less than at right angles, behavior which at atmospheric pressure would be classed as abnormal. Apparently wave mechanics is hardly yet in a position to undertake detailed calculations of the resistance of crystals in different directions, particularly under pressure. Single crystal tin in two orientations decreases smoothly in resistance over the entire range, with practically no change in the ratio of resistance in different directions. Single crystal antimony is the only known example of a metal whose resistance passes through a maximum with increasing pressure. This maximum occurs at lower pressures the more nearly the axis is perpendicular to the length, and the pressure of the maximum is a strong temperature function. Single crystal tellurium decreases in resistance under a pressure of 30,000 kg/cm<sup>2</sup> by a factor of the order of 600. It appears that at a pressure only slightly beyond 30,000 the temperature coefficient of resistance will reverse sign, becoming positive like a metal.

The resistance of bismuth at the I-II transition takes a downward jump by a factor of about 6, but at the II-III transition the resistance jumps up by a factor of about 2.5 against the change of volume. The only other example of a change of resistance against the change of volume is caesium, for which, however, the jump in resistance is comparatively small. The pressure coefficients of modifications II and III of bismuth are normal (negative), in spite of the fact that bismuth I is abnormal (positive coefficient). The behavior of bismuth is to be contrasted with that of caesium and barium, where a modification with positive coefficient transforms to another modification with only slightly different positive coefficient.

I am indebted, for financial assistance in this work to the Milton Fund of Harvard University, and to Mr Charles Chase for skillful assistance in constructing and setting up the apparatus. Early publication of this paper was made possible by the Francis Barrett Daniels Fund of Harvard University.

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#### REFERENCES

- <sup>1</sup> P W Bridgman, Proc Amer Acad **70**, 71-101, 1935
- <sup>2</sup> P W Bridgman, *The Physics of High Pressure*, Bell, London, and Macmillan, New York, 1931
- <sup>3</sup> P W Bridgman, Phys Rev **48**, 893-908, 1935, Proc Amer Acad **72**, 40-138, 1937
- <sup>4</sup> P W Bridgman, Proc Amer Acad **71**, 387-400, 1937, and also second reference under 3
- <sup>5</sup> Particularly second reference under 3, page 49
- <sup>6</sup> P W Bridgman, Proc Amer Acad **67**, 321-343, 1911
- <sup>7</sup> P W Bridgman, Proc Amer Acad **70**, 82, 1935
- <sup>8</sup> P W Bridgman, Proc Amer Acad **47**, 441-558, 1912
- <sup>9</sup> P W Bridgman, Proc Amer Acad **68**, 95-123, 1933
- <sup>10</sup> P W Bridgman, Proc Amer Acad **52**, 573-646, 1917
- <sup>11</sup> P W Bridgman, Proc Amer Acad **67**, 305-344, 1933, also 10
- <sup>12</sup> P W Bridgman, Proc Amer Acad **64**, 75-90, 1930
- <sup>13</sup> P W Bridgman, Proc Amer Acad **60**, 385-421, 1925
- <sup>14</sup> P W Bridgman, Proc Amer Acad **58**, 61-154, 1921
- <sup>15</sup> E Grüneisen, *Handbuch der Physik*, **13**, 10 (1928)
- <sup>16</sup> P W Bridgman, Proc Amer Acad **62**, 215, 1927
- <sup>17</sup> P W Bridgman, Proc Amer Acad **47**, 347-438, 1911
- <sup>18</sup> O Sckell, Ann d Phys **6**, 932-956, 1930
- <sup>19</sup> Reference 9, p 99
- <sup>20</sup> Reference 9, p 101

- <sup>21</sup> Reference 9, p 106
- <sup>22</sup> P W Bridgman, Phys Rev **48**, 831, 1935
- <sup>23</sup> Reference 12, p 86
- <sup>24</sup> First reference under 3, p 895
- <sup>25</sup> Reference 9, p 114
- <sup>26</sup> First reference under 3, p 890



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**ROUGH COMPRESSIBILITIES OF FOURTEEN  
SUBSTANCES TO 45,000 Kg/Cm<sup>2</sup>**

**BY P. W. BRIDGMAN**

**INVESTIGATIONS ON LIGHT AND HEAT MADE WITH AID FROM THE RUMFORD FUND**



# ROUGH COMPRESSIBILITIES OF FOURTEEN SUBSTANCES TO 45,000 Kg/Cm<sup>2</sup>

BY P. W. BRIDGMAN

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## INTRODUCTION

In two preceding papers<sup>1</sup> the parameters of a number of transitions have been determined up to 45,000 kg/cm<sup>2</sup>. The method consists in determining at various temperatures the discontinuity in volume by measuring the displacement of the piston by which pressure is produced. If instead of determining the discontinuity in the motion of the piston, one plots the motion of the piston at constant temperature as a function of pressure, one obviously has a rough measure of the compressibility. Various corrections, however, reduce the accuracy of the method and restrict its applicability to the more compressible substances. It probably will be possible to improve the method, and in fact I now have under construction an apparatus which should permit better values. But in the meantime, because of their intrinsic interest, I give in the following pages rough results for some of the more compressible substances, for which the results should be most accurate.

## TECHNIQUE AND CORRECTIONS

If the contents of a cylindrical container are subjected to pressure by the thrust of a piston, the total displacement of the piston is evidently determined by the compression of the contents, the distortion of the container, and the distortion of the piston and packings. If the contents possess much mechanical stiffness, then friction on the walls produces a stress system in the contents which is not a hydrostatic pressure, and the interpretation of the piston displacement is not clear. The first requirement, therefore, is to make the pressure approximately hydrostatic. This was accomplished by enclosing the material under measurement in a lead sheath. The general arrangements are indicated in Figure 1, drawn to scale. They are practically the same as for the transition measurements. In the previous paper a discussion was given of the distortion of the container under pressure adequate for the purposes of that paper, but here the requirements are more exacting, and a more elaborate examination is necessary. Suppose, for example, that an incompressible substance is compressed in a cylinder to such a pressure that the increase of cross section of the container is 10 per cent. If now a transition occurs, and the change of volume is measured by measuring the displacement of the piston, a 10 per cent error will be made in the  $\Delta V$  of the transition if no correction is made for the change of cross section. But on the other hand, before the transition occurs a 10 per cent compression would have been ascribed to the substance if no correction had been made for the cross section, whereas the actual compression was zero. That is, an infinite error in the compression against a 10 per cent error in the volume change of the transition is here the result of improperly correcting for the distortion of the container.

An exact evaluation of the corrections is out of the question. Not only are the boundary conditions incapable of exact formulation, but the stresses are beyond the range in which linearity holds between stress and strain, and there is marked hysteresis. The latter effect should be approximately eliminated by using the mean of measurements with increasing and decreasing pressure. The elastic deformation was dealt with by computing it for idealized conditions, and then manipulating the results to secure agreement with certain check measurements. The idealized elastic problem is that of the infinitely long cylinder under external and internal hydrostatic pressure, the inner and outer radii being taken as those at mean positions along the axis of the cone. The external pressure can be evaluated, as explained in the previous paper, from measurements of the longitudinal

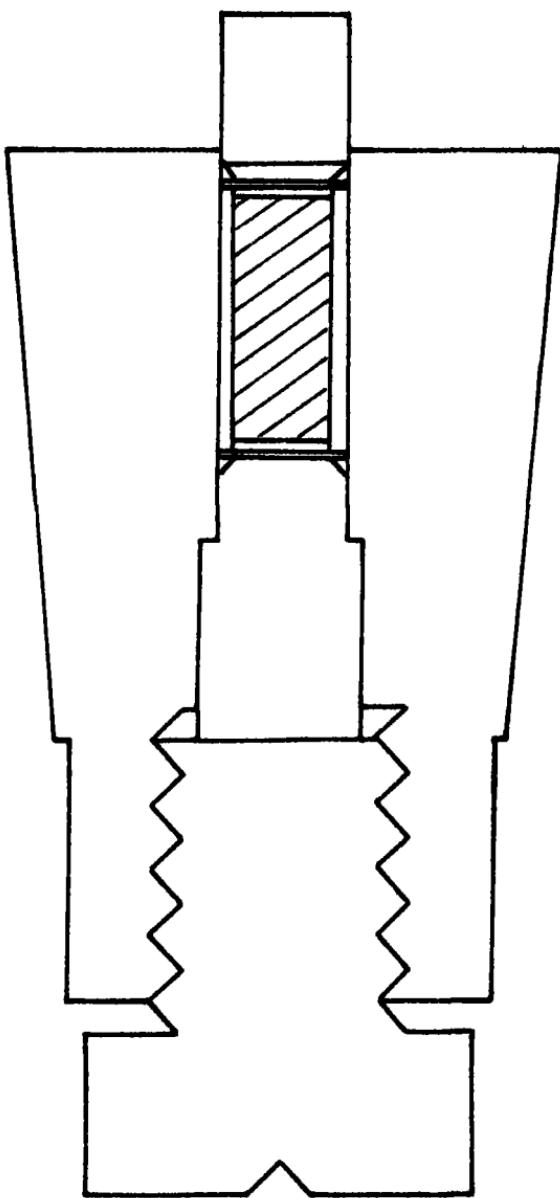


FIGURE 1 Shows the method of mounting the specimen (cross hatched) in a lead sheath for compressibility measurements

displacement of the cone into the sleeve, which gives the means for evaluating the friction. The idealized infinite cylinder fails to correspond to the actual case not only because of the conical figure of the actual container, but also because of the closures at the ends, one end carrying the freely moving plunger and the other end being closed by a screw plug which transmits a longitudinal tension to the walls of the container. On the outside of the container there is a longitudinal shearing force which gets transformed into a mean longitudinal tension inside. The distortion of an infinite cylinder under longitudinal tension can be calculated, and crude allowance made for these effects. Then there is the very important effect of finite length, the length of the cavity was on the average 2.5 times the diameter. This means that very effective support is afforded by the ends, which are not exposed to the internal pressure, although exposed to external pressure. As a result the cavity must become somewhat barrel shaped, and the cross section at the piston is different from that at the center of the cavity. In an infinite cylinder a simple application of Betti's theorem shows that the increase of cross section at the piston is only one half as great as that further down in the cavity. This means that the effective correction of the cross section that is to be used for computing the pressure from the thrust on the piston is of the order of only one half the correction on the cross section from which the total change of volume is to be computed.

There are two independent measurements that can be made to check any computations. The longitudinal displacement of the container into the collar can be measured as a function of the thrust on the piston, and the internal change of volume can be measured when there is no internal pressure but the external pressure is made to be approximately the same as in the actual experiment by exerting on the whole container the same total thrust as that which in the actual experiment is exerted on the piston. This latter change of internal volume was measured by sealing a graduated capillary into the cylinder, which was filled with mercury, and observing the motion of the mercury column in the capillary as a function of thrust. The longitudinal displacement into the collar agreed exactly with that computed. The change of internal volume was 0.8 of that calculated for the infinite cylinder, the difference is to be ascribed to the effects due to the unknown distribution of longitudinal stress, departure from cylindrical figure, etc. The calculated corrections for the effect of internal and external pressure together were therefore reduced by this factor of 0.8. An additional reduction factor of 0.9 was guessed

at to allow for the difference of terminal conditions in the two cases, making a total reduction factor on the correction calculated for the infinite cylinder of 0.7. The final correction assumed for the maximum pressure ( $50,000 \text{ kg/cm}^2$ ) was 2.7 per cent on the effective area from which the compression was calculated, and 1.5 per cent on the area from which pressure was calculated. These corrections were taken to be linear with pressure.

As actually used, this was a differential method, similar to that which I had used to measure the compressibility of liquids,<sup>2</sup> and which has been extensively used at the Geophysical Laboratory in Washington in measuring the compressibility of solids.<sup>3</sup> The cylinder was filled with the substance under investigation in its lead sheath, and the displacement of the piston determined as a function of pressure. This was done on a careful time schedule. Pressure was first increased to the maximum in steps of 10,000 at intervals of 1 minute, released to 0 and again increased to the maximum on the same time schedule. This constituted the preliminary seasoning. Pressure was now released to 0 and increased back to the maximum in steps of 2,000 on a 1 minute schedule. This run down and up in 25 steps each way and in 50 minutes altogether constituted the essential part of the measurements. Pressure was finally reduced to 0 in 10,000 steps on the 1 minute schedule and the apparatus taken apart. It was now set up again with a core of soft steel replacing the previous substance, in a lead sheath of approximately the same size as at first. The same sequence of measurements was now made on the lead and steel. Next the differences of corresponding displacements of the two runs were computed, plotted on large size paper, and a single curve drawn as the mean of ascending and descending branches. A detailed discussion of the effects of friction, which I will not take space to give here, showed that it is better to take the differences of ascending and descending branches of the two curves, and then draw the mean curve of the loop thus obtained, rather than to draw the mean curves for the two loops and then take the difference of the mean curves.

The upper end of the loops require somewhat special treatment. Figure 2 shows how the top of the loop runs horizontally on release of pressure during an interval corresponding to the friction on the piston. In taking the mean loop, this frictional effect was eliminated as best it might by extrapolating the curve AC beyond C graphically, and using the mean of this extrapolated curve and AB in the pressure interval CB.

The maximum pressure listed in the following is  $45,000 \text{ kg/cm}^2$ ,

corresponding roughly to the mean between the pressures at C and at B. The maximum pressure on the piston was more than 50,000, but friction reduced this in the material under measurement. It would have been easy to extrapolate from the results to an effective maximum pressure of 50,000, but there is no reason why the reader should not make this extrapolation to suit himself.

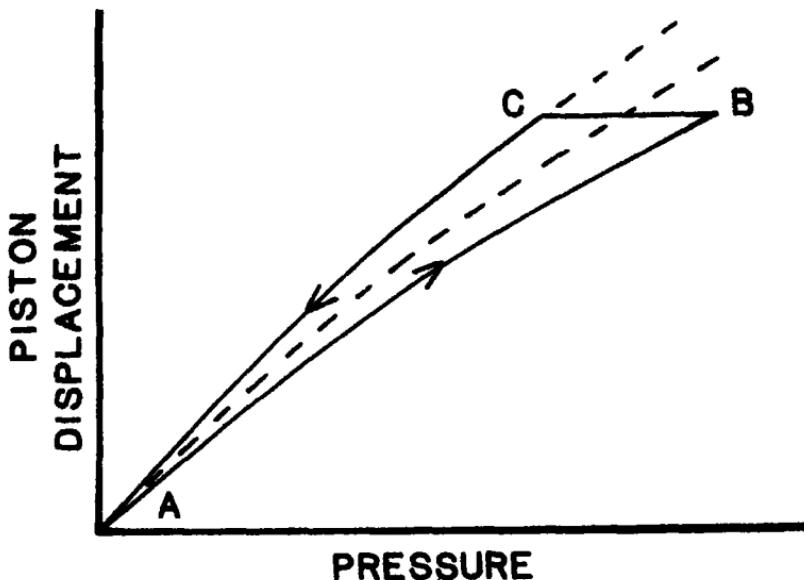


FIGURE 2 Identized plot of piston displacement against pressure

The final result was a smooth curve corresponding to the difference of compressibility between the substance under investigation and iron. Since the compressibility of iron is small compared with that of the other substance, I assumed for the compressibility of iron values extrapolated from my previous measurements to 12,000. I had formerly found by direct measurement up to 12,000 at 30° for the compressibility of iron.

$$-\Delta V/V_0 = 5.87 \times 10^{-7} p - 2.37 \times 10^{-12} p^2,$$

$p$  in kg/cm<sup>2</sup>. Since in the following all quantities of material were determined by weighing, what is needed is the compression of iron in cm<sup>3</sup> per gm. The following were assumed to be the compressions in cm<sup>3</sup> of 1 gm of iron at pressures of 10,000, 20,000, 30,000, 40,000, and

50,000 kg/cm<sup>2</sup> respectively 0.00072, 0.00137, 0.00196, 0.00250, and 0.00298.

Since it was not usually convenient to use exactly the same amounts of lead in the actual and the blank runs, the compression of the differential amount of lead also entered as a correction. The compression of lead to 45,000 was determined by direct measurement by filling the container entirely with lead. The following are the values found for the compression in cm<sup>3</sup> per gm at 10,000, 20,000, 30,000, 40,000, and 50,000 respectively 0.0020, 0.0036, 0.0051, 0.00635, and 0.0075. The previous measurements up to 12,000 could be reproduced by a second degree formula. The previous measurements were 0.0019 at 10,000 and 0.0035 extrapolated to 20,000. The agreement is not bad. Beyond 20,000 the second degree formula representing the former results goes off badly, at 50,000 giving a change of volume of 0.0060 against 0.0075 experimental. The change of volume thus actually proceeds at a more rapid rate than the second degree formula would indicate. This is as is to be expected, because the second degree formula demands a minimum compression and a reversal at very high pressures.

The useful life of one of the containers was rarely as much as ten applications of the maximum pressure. In the transition measurements 20 applications were not unusual. The conditions here were more exacting, however, and much closer track was kept of the progress of permanent distortion. A special arrangement was made for measuring the internal diameter of the container at different points along the axis to an accuracy of 0.0001 inch, and after every completed run the container was remeasured for permanent distortion, and discarded, or else reamed to a slightly larger size, when the permanent stretch got as high as 0.002 inch, which experience showed to be about the maximum tolerable. It would have been very convenient if it had been possible to make the blank runs on iron and lead on a single container once and for all, but this did not prove to be possible, since the containers were not sufficiently reproducible. This made it necessary to make a blank run with each new container. On the average a container yielded results for the compression of only one substance. If it had been possible to get reproducible containers, results could have been obtained twice as fast and with twice as great an economy in containers.

A great deal of preliminary work was put into getting the best details of the various manipulations, such as the time schedules etc., to give most reproducible results. In the preliminary work a good

many measurements were made on the same substance, but after the method was established, one or two set-ups usually sufficed. A check on the accuracy of the measurements is afforded by comparing with the results previously obtained up to 12,000 and in some cases to 20,000. The low pressure end of the range was in general much less accurate than the high pressure end, in many cases the results were adjusted so as to agree with previous results over the first 5,000 kg/cm<sup>2</sup>.

The detailed results now follow.

#### DETAILED RESULTS

*Lithium* One set-up was made for this substance, with the corresponding blank run. In Table I is given the compression at room

TABLE I  
COMPRESSION OF THE ALKALI METALS

#### Compressions

Pressure kg/cm <sup>2</sup>	Lithium cm <sup>3</sup> /0 534gm	Sodium cm <sup>3</sup> /0 971gm	Potassium cm <sup>3</sup> /0 870gm	Rubidium cm <sup>3</sup> /1 532gm	Ceasium cm <sup>3</sup> /1 88 gm
5,000	043	071	116	164	0 182
10,000	074	117	183	238	271
15,000	101	148	230	279	326
20,000	125	182	268	316	372
23,000					{ 398
25,000	145	209	301	345	420
30,000	165	233	329	371	438
35,000	184	254	353	393	464
40,000	202	273	375	413	487
45,000	218	290	396	431	507

\* Phase change

temperature of that amount of material which occupies 1 cm<sup>3</sup> under normal conditions. Some check on the results can be obtained by comparison with previous measurements up to 20,000.<sup>4</sup> Previous measurements of the compression at 10,000 and 20,000 were 0.073 and 0.123 against 0.074 and 0.130 found now.

*Sodium* Three different set-ups were made with three corresponding blank runs. One of the blanks was made with lead and gold instead of lead and iron, the idea being that gold might be so much softer than iron as to result in the pressure being appreciably more hydrostatic throughout the container, but no superiority of this run was found over that with iron, and gold was not tried in other blanks.

There was no consistent difference between the results of the three runs, the one which gave the lowest compression at 20,000 gave the highest at 45,000. The results are given in Table I. The low pressure results were adjusted to agree with the former ones<sup>6</sup> at 10,000. At 20,000 the change of volume now found is 0.183 against 0.189 found before. The direction of deviation is the same as for lithium. The former results are doubtless to be preferred. I do not think, however, that this means necessarily an error in the same direction at the highest pressures of the range, but I think it probable that the effect is connected with hysteresis, and that the maximum error might be looked for at the center of the range. This would mean that the relation found in all the work described in this paper between pressure and change of volume is probably a little too nearly linear, the actual compressibility dropping more rapidly at high pressures than found here.

*Potassium* One set-up was made, but runs were made at three temperatures room temperature, 75°, and 125°, in an attempt to find the temperature coefficient of compressibility (or the pressure coefficient of thermal expansion). The method proved not to be sensitive enough, however, and after some experimenting I abandoned the attempt to get this sort of information out of the measurements. The blank run was made with tungsten and lead instead of iron and lead as usual. The compressibility of tungsten is less than that of iron, and for this reason it is ideally a better material for the differential measurements. But the second degree term in my previous measurements for tungsten<sup>6</sup> is perhaps not quite as certain as for iron, so that extrapolation from 12,000 to 50,000 is more hazardous. The compressibility of potassium is so high, however, that there should be no appreciable error here.

The results are shown in Table I. The value at 5,000 was made to agree with the former measurements. At 10,000 and 20,000 the present values of compression are 0.183 and 0.268 respectively against 0.189 and 0.277 found formerly<sup>7</sup>.

*Rubidium* Runs were made with two different set-ups, with the second set-up six different runs were made at temperatures between 0° and 75°. The important point at issue was whether rubidium has a transition like that which had just been found for caesium. At first, slight irregularities were found which were favorable to the interpretation of a small transition, but nothing was found that would definitely repeat, and I do not believe that there is a transition up to 45,000 with a volume change as large as 0.00015 cm<sup>3</sup>/gm.

The two different set-ups gave fairly concordant results for the compression, the greatest discrepancy being at 45,000, where the results were 0.433 and 0.428. The mean results of the two set-ups are given in Table I. The compression at 5,000 was adjusted to agree with the former value<sup>8</sup> at 50°, this being the only temperature at which measurements had been previously made. The present values for the compressions at 10,000 and 15,000 are 0.233 and 0.279 respectively, against 0.234 and 0.279 formerly.

*Caesium.* Runs were made with a single set-up at room temperature. Caesium has a fairly small but perfectly clean cut transition at 23,000 kg/cm<sup>2</sup>. At room temperature the transition pressure reached from above and below was not appreciably different. The mean change of volume differed by only 2 per cent from that with either increasing or decreasing pressure, namely 0.0084 cm<sup>3</sup> per 1.88 gm, or 0.0034 cm<sup>3</sup>/gm (1.88 is the density under standard conditions).

The results are given in Table I. Previous measurements<sup>9</sup> to 15,000 were made only at 50°, so there is no exact basis for comparison. Present values for  $\Delta V$  per 1.88 gm at 5,000, 10,000, and 15,000 are 0.182, 0.271, and 0.326 respectively against 0.184, 0.269, and 0.328 formerly. The present value at 5,000 was adjusted to agree with my estimate of what the previous value would have been corrected to room temperature. The transition pressure has also been determined by the discontinuity in resistance, the value found in this way was 22,000 against 23,000 above.

*Calcium.* The material was some on which I had made compressibility measurements many years ago,<sup>10</sup> probably, although not certainly, from the General Electric Co. It is not as pure as other material from the same source on which I have recently made resistance measurements, or as another sample formerly used also for compressibility.

Runs were made with a single set-up at room temperature, 75°, and 125°. Runs were made at different temperatures in the search for a transition, which had been suggested by previous measurements of shearing strength.<sup>11</sup> In fact, the shearing measurements suggested two transitions. In this work persistent irregularities of the right character were found both with increasing and decreasing pressure at all three temperatures, and it is highly probable that there are one or more transitions. The total change of volume is of the order of 0.0008 cm<sup>3</sup>/gm. The pressures of transition are between 25,000 and 36,000, the sensitivity was not great enough to definitely resolve the irregularities, and good results for the variation with temperature were not found. Previous shearing results indicated the mean pressure of the

transition or transitions as 30,000. Recent measurements of the resistance of calcium to 30,000 have shown no discontinuity up to this pressure, there is nothing inconsistent in this with the existence of a transition, because even if the transition exists below 30,000 it might have been suppressed by viscous resistance.

The results are shown in Table II. No attempt is made in the

TABLE II  
COMPRESSION OF THE ALKALI EARTH METALS

Pressure kg/cm <sup>2</sup>	Calcium cm <sup>3</sup> /1 538 gm	Strontium cm <sup>3</sup> /2 629 gm	Barium cm <sup>3</sup> /3 62 gm
5,000	0.031	0.047	0.045
10,000	0.058	0.075	0.086
15,000	0.082	0.099	0.121
20,000	0.103	0.122	0.159*
25,000	0.122	0.136	0.186
30,000	0.130	0.155	0.209
35,000	0.155	0.172	0.230
40,000	0.171	0.188	0.250
45,000	0.188	0.204	0.269

\* Phase change

Table to suggest any transition, but the results are smoothed right across the irregularities. The volume decrements at 5,000, 10,000, and 20,000 of the present work are 0.031, 0.058, and 0.103 respectively. Previous results on the most nearly comparable sample were 0.029, 0.055, and 0.099 respectively. The present values are consistently higher than the old, the discrepancy thus being in the opposite direction from that of the alkali metals. Impurity of strontium or barium in the present sample would account for the direction of discrepancy.

**Strontium** The material was from Eimer and Amend, probably not of very high purity, and the same as that used in recent measurements of the resistance to 30,000. Runs were made with a single set-up at three temperatures room temperature, 75°, and 125°. The runs were made on the one minute, 2,000 kg schedule. There is quite unmistakably a transition at all three temperatures, but it is unusually difficult to start the transition, the pressures at which the transition starts with increasing and decreasing pressure being separated by an unusually large amount. Furthermore, when the transition starts it

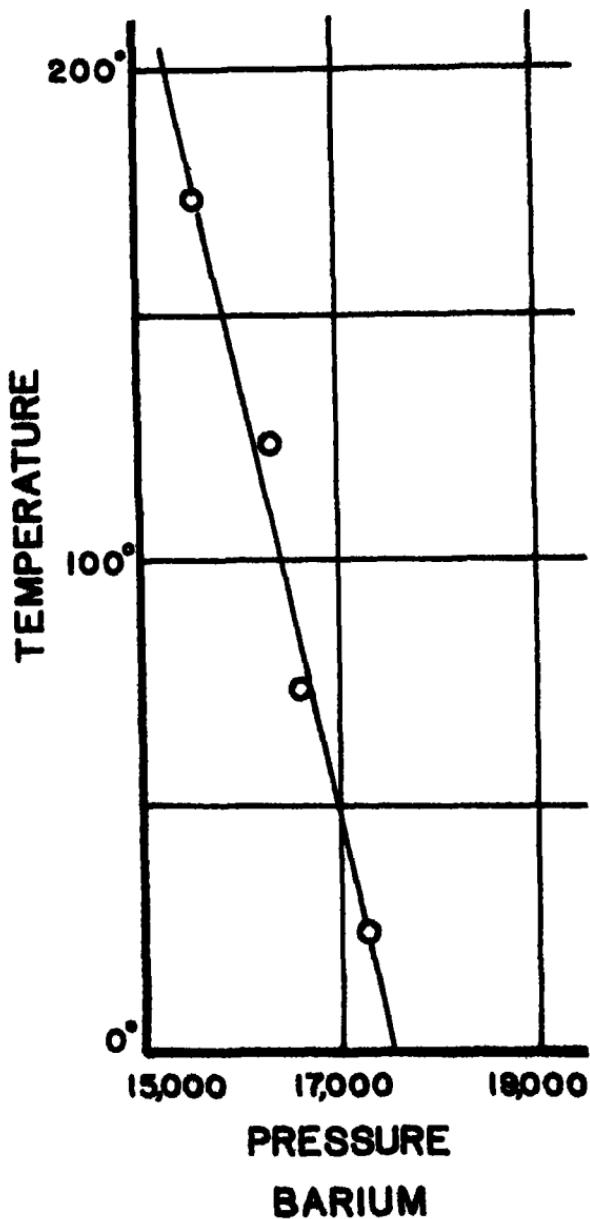


FIGURE 3 Shows the transition temperatures of barium as a function of pressure in kg/cm<sup>2</sup>

runs very sluggishly, so that with the time schedule employed the transition is running through an unusually wide pressure interval. At the three temperatures, 25°, 75°, and 125°, the respective pressures at which the transition started with increasing pressure was 38,000, 34,000, and 33,000, and with decreasing pressure the corresponding pressures were 19,000, 19,000, and 18,000. The mean change of volume is 0.0034 cm<sup>3</sup>/gm, or fractionally 0.0091 on the initial volume. The measured change of volume was less on increasing pressure than on decreasing, which means that the high pressure phase is more compressible than the low pressure phase, the normal direction of

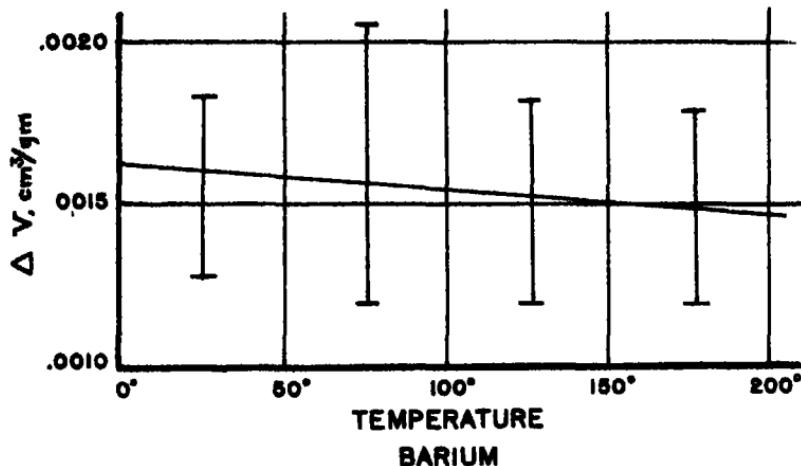


FIGURE 4 The volume changes when barium undergoes transition as a function of temperature along the transition line

difference. The difference of compressibility is such that in the pressure interval from 17,000 to 43,000 the high pressure phase is compressed by 0.0066 more than the low pressure phase.

The compressions of the low pressure phase are given in Table II, above the pressure of the transition the values are extrapolated with the help of the measured volumes of the high pressure phase. The data already given for the transition may be made to yield the volumes of the high pressure phase above the transition point. The compression at 10,000 was adjusted to agree with the former value.<sup>12</sup> After making this adjustment, the volume at 5,000 is not in at all good agreement with the previous value,  $\Delta V$  being 0.047 against 0.039 formerly. There is no reason to suspect, however, that this means that the high pressure values are any less reliable than usual.

**Barium** The material was from Mackay, and was the same as that used in recent measurements of the resistance to 30,000. Runs were made with a single set-up, and at room temperature, 75° twice, 125°, and 175°. Barium has a perfectly definite transition, running much more sharply and within much narrower pressure limits than strontium. A previous attempt to find a transition of barium with the volumetric apparatus had given negative results,<sup>13</sup> the apparatus has since been very much improved. The transition pressures and temperatures are shown in Figure 3, the change of volume in Figure 4, and the transition parameters in Table III.

TABLE III  
TRANSITION PARAMETERS OF BARIUM

Pressure kg/cm <sup>2</sup>	Temperature °	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
17,500	0°	-0.0008	0.0163	4.90	115
16,400	100°	-0.0008	0.0155	6.37	150
15,300	200°	-0.0008	0.0147	7.65	180

The compressions are given in Table II, the low pressure phase below 15,000, and the high pressure phase above. The compression was adjusted to agree with the former value<sup>14</sup> at 5,000. The present values at 10,000 and 15,000 are 0.088 and 0.124 respectively, against 0.089 and 0.124, good agreement.

**Indium** The material was inherited from Professor T. W. Richards, and was of high purity. Runs were made with a single set-up at room temperature, 75°, and 125°. There were persistent irregularities at all temperatures that probably mean two or three small transitions, the highest transition pressure is probably in the neighborhood of 40,000, and the lowest around 30,000. The change of volume of the largest transition is probably not more than 0.0002 cm<sup>3</sup>/gm, with the others not more than half this.

The volume compressions are given in Table IV, no adjustment was made in any of the low pressure values. For comparison there is only a measurement by Richards<sup>15</sup> at pressures up to 500 kg/cm<sup>2</sup>, who found 0.027 for the initial compressibility, consistent enough with the present values.

**Tin** Runs were made with a single filling at room temperature, 100°, and 125°. Previous measurements of shearing<sup>16</sup> suggested a transition, but previous measurements in the volumetric apparatus<sup>17</sup> had given negative results. The volume apparatus was now so much

improved that it seemed worth while to repeat the exploration, but no satisfactory evidence of a transition was found.

The compressions are given in Table IV. No adjustment of values was made at low pressures. The present compressions at 5,000, 10,000, and 20,000 are 0.010, 0.020, and 0.038 respectively, against 0.009, 0.017, and 0.032 former<sup>18</sup> (the last value extrapolated with the second degree formula). The shape of the volume curve is thus somewhat different from that found before. The compressibility of tin is so small that the method is becoming incapable of such relatively accurate results as for most other substances, there is no question but that the previous lower values are to be preferred.

*Lead* The measurements on this have already been described in connection with the blank runs. The compressions in terms of the initial volume (that is, cm<sup>3</sup> per 11.35 gm) are given in Table IV.

TABLE IV  
COMPRESSION OF FOUR MISCELLANEOUS ELEMENTS

Pressure kg/cm <sup>2</sup>	Compressions			
	Inium cm <sup>3</sup> /7.43 gm	Tin cm <sup>3</sup> /7.30 gm	Lead cm <sup>3</sup> /11.35 gm	Sulfur cm <sup>3</sup> /2.07 gm
5,000	0.12	0.10	0.12	0.49
10,000	0.24	0.20	0.23	0.84
15,000	0.35	0.29	0.32	1.10
20,000	0.45	0.38	0.41	1.31
25,000	0.54	0.48	0.50	1.48
30,000	0.64	0.57	0.58	1.62
35,000	0.73	0.66	0.65	1.75
40,000	0.82	0.75	0.72	1.86
45,000	0.91	0.84	0.79	1.95

*Sulfur* Runs were made with a single set-up at room temperature and 125°. Previous attempts to find a transition had been negative,<sup>19</sup> the present measurements were made with the idea that perhaps with the improved apparatus a transition would now be found. There were irregularities in the neighborhood of 25,000 such as to make a transition not impossible, but I regard it as improbable. If there is one, its  $\Delta V$  is not more than 0.0003 cm<sup>3</sup>/gm.

The values of the compression are given in Table IV. Previously I have made measurements on the linear compressibility in different directions of the single crystal up to 12,000, from which the volume compression may be computed. Agreement with the present values

is exact to two significant figures, the usual adjustment of the low pressure values to secure agreement at some point was not made.

*Carbon Dioxide.* Measurements were made on this because of the desire of Dr H Spener to secure experimental values of compression with which to check some theoretical calculations.<sup>20</sup> Runs were made with a single set-up, two at solid CO<sub>2</sub> temperature, one at 0°, and one at room temperature. The apparatus was filled at liquid air temperature, and an initial pressure of 10,000 kg/cm<sup>2</sup> was applied at this temperature in order to get the CO<sub>2</sub> into a region where it would not leak at higher temperatures. The first application of pressure at solid CO<sub>2</sub> temperature seemed to go without any hitch, but after this there was internal evidence that there may have been slight leak at two or three places. The blank run from which the differential compressibility was determined was made at room temperature, at solid CO<sub>2</sub> temperature the friction of the external surface of the cone is

TABLE V  
COMPRESSION OF TWO COMPOUNDS  
Compressions

Pressure kg/cm <sup>2</sup>	CO <sub>2</sub> Fractional	Na Cl cm <sup>2</sup> /2 18 gm
5,000	091	020
10,000	142	037
15,000	177	052
20,000	206	066
25,000	226	078
30,000	246	089
35,000	262	099
40,000		108
45,000		118

much greater than at room temperature, so that there is possibly an error from this factor as well as from the difference of temperature. Furthermore, it was not feasible to determine the quantity of CO<sub>2</sub> by weighing as usual, but it had to be found from measurements of the initial volume. There are several factors, therefore, making the accuracy of these measurements less than usual, but the absolute compressibility of CO<sub>2</sub> is high, and since apparently there are no previous measurements at all, it seemed to me that the rough measurements were worth while.

The numerical values of compression are given in Table V. These run to only 35,000 kg/cm<sup>2</sup>. There is no doubt that at high pressures,

25,000 or higher, there is a transition. This runs sluggishly, and is spread over a considerable pressure range. The fractional  $\Delta V$  may be as high as 0.003, or perhaps even higher. In view of the various uncertainties, I did not feel justified in attempting to force the results to give the compression of the high pressure phase above 35,000.

*Sodium Chloride.* Runs were made with a single set-up, at room temperature only. Previous explorations<sup>21</sup> had made it pretty certain that there is no transition up to nearly 50,000, so that runs at other temperatures were not necessary.

The compressions are given in Table V. The value at 5,000 was adjusted to agree with the previous value<sup>22</sup> obtained when making measurements to 12,000. The present values at 10,000 and 20,000 are 0.037 and 0.066 respectively, against 0.037 and 0.064, the latter value being extrapolated by the second degree formula. The agreement at 10,000 is exact, and at 20,000 the difference is in the direction to be expected in view of the fact that the second degree formula which fits the results to 12,000 gives a minimum in volume at 41,000.

### DISCUSSION

The methods of wave mechanics are now so far advanced that it is possible to make fairly satisfactory calculations of compressibilities, at least for the simpler substances. The value of any check of the calculations against experiment is greater the greater the range of the volume change that can be covered by experiment, so that these results should prove particularly useful in giving an idea of the relative importance of the various effects considered by the theory. Theoretical calculations of this sort have been made by Dr J Bardeen, and are now in course of preparation for publication. In the case of the alkali metals it is possible to obtain rather good agreement with experiment over the entire range, the agreement is best for caesium, and becomes less good as one moves toward lithium. It turns out that by far the greater part of the compression of caesium is a phenomenon involving the ionic forces in the metal, which are comparatively easy to compute, whereas as one proceeds towards lithium, the electronic interaction terms, which are more difficult to compute, become more important. I shall not attempt myself to go further into the theoretical significance of the results.

There is, however, one matter of a more empirical nature which is of interest. Recently Murnaghan<sup>23</sup> has modified the classical theory of elasticity in such a way that it is capable of dealing rigorously with the relation between stress and strain for finite strain. Of course

when the functional relation between stress and strain is written out explicitly for any particular substance it is not possible to avoid the entrance of empirical constants, such as the coefficients of a power series expansion, but even with this limitation it seems that the form of the function which naturally presents itself in Murnaghan's analysis is better adapted to represent the relation between volume and pressure than many formulas which have been previously used, and therefore is more desirable if short range extrapolation has to be made. Murnaghan's relation between pressure and volume for those cases where two empirical constants are necessary<sup>14</sup>

$$p = af + bf^2,$$

where  $f = \frac{1}{2} \{(1 - 1/V)^2 - 1\}$ , and  $a$  and  $b$  are constants to be determined empirically.

This formula may be checked as an extrapolation formula. I have made the calculations for caesium, lithium, and sulfur. The tables already given enable  $f$  to be determined as a function of pressure. Then  $a$  and  $b$  were determined so as to agree with experiment at 10,000 and 20,000 kg/cm<sup>2</sup>. The value of  $f$  at 45,000 was then substituted into the formula, and the corresponding value of  $p$  calculated. Perfect agreement would demand that the calculated  $p$  be 45,000. The values actually found were 44,992, 45,320, and 48,870 respectively for caesium, lithium, and sulfur. The agreement is astonishingly good for caesium and lithium, and still much better than I had expected for sulfur. Murnaghan's formula should, therefore, have much usefulness. I think, however, that too much theoretical significance cannot be attached to the success of the formula. The constants  $a$  and  $b$  have evidently only an empirical significance, and in fact  $a$  and  $b$  may have the same or opposite signs in order to fit the experimental points at 10,000 and 20,000. It seems probable to me that the formula in large part owes its success to its mathematical form, which is such that the volume goes to zero when pressure goes to infinity. Many of the equations of state of the past have represented the volume as approaching some finite value at infinite pressure. This is contrary to what we would expect now in the light of our knowledge of the structure of the atom, and is also definitely contrary to the experimental evidence, for the volume at high pressure almost always drops off more rapidly than would be indicated by extrapolation according to the usual formulas from experimental values at low pressures. This would suggest, therefore, that any extrapolation formula giving

zero volume at infinite pressure would have a fair chance of success I have tried a simple formula of this type for caesium, namely

$$\mu = a (V_o/V - 1) + b(V_o/V - 1)^2$$

If  $a$  and  $b$  are determined to agree with experiment at 10,000 and 20,000 and are then used in extrapolating,  $\mu$  calculates to 43,300 where it should be 45,000, not bad agreement

It is a pleasure to acknowledge financial assistance with regard to the execution of the experiments from the Rumford Fund of the American Academy, the Milton Fund of Harvard University, and the Carnegie Institute. I am also indebted to the Francis Barrett Daniels Fund of Harvard University for assistance with the publication. For most of the readings I am indebted to Mr L H Abbott.

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#### REFERENCES

- <sup>1</sup> P W Bridgman, Phys Rev **48**, 893-906, 1935 Proc Amer Acad **72**, July, 1937
- <sup>2</sup> P W Bridgman, Proc Amer Acad **49**, 1-114, 1913
- <sup>3</sup> L H Adams and E D Williamson, Jour Frank Inst **195**, 475, 1923
- <sup>4</sup> P W Bridgman, Proc Amer Acad **70**, 91, 1935
- <sup>5</sup> Reference (4), p 93
- <sup>6</sup> P W Bridgman, Proc Amer Acad **58**, 181, 1923
- <sup>7</sup> Reference (4), p 95
- <sup>8</sup> P W Bridgman, Proc Amer Acad **60**, 394, 1925
- <sup>9</sup> Reference (8), p 402
- <sup>10</sup> Reference (6), p 199
- <sup>11</sup> P W Bridgman, Phys Rev **48**, 837, 1935
- <sup>12</sup> Reference (6), p 201
- <sup>13</sup> First reference under (1), p 903
- <sup>14</sup> P W Bridgman, Proc Amer Acad **62**, 215, 1927
- <sup>15</sup> T W Richards
- <sup>16</sup> Reference (11), p 839
- <sup>17</sup> First reference under (1), p 903
- <sup>18</sup> Reference (6), p 211
- <sup>19</sup> First reference under (1), p 903
- <sup>20</sup> H Sponer and M Bruch-Willstätter, Jour Chem Phys **5**, 745-751, 1937
- <sup>21</sup> First reference under (1), p 906
- <sup>22</sup> P W Bridgman, Proc Amer Acad **64**, 33, 1929
- <sup>23</sup> F D Murnaghan, Amer Jour Math **59**, 235-260, 1937



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**POLYMORPHIC TRANSITIONS UP TO 50,000 Kg/Cm<sup>2</sup> OF  
SEVERAL ORGANIC SUBSTANCES**

**By P. W. BRIDGMAN**

**INVESTIGATIONS ON LIGHT AND HEAT MADE WITH AID FROM THE RUMFORD FUND**



# POLYMORPHIC TRANSITIONS UP TO 50,000 Kg/Cm<sup>2</sup> OF SEVERAL ORGANIC SUBSTANCES

By P W BRIDGMAN

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## INTRODUCTION

This paper continues the subject already treated in Proceedings of the American Academy of Arts and Sciences, vol 72, July 1937 In that paper the transitions of some 35 substances, all of them inorganic, were examined In this paper the examination is extended to

organic substances. The apparatus and the technique were the same as before, so that no new discussion is needed. In general comment on the new results, it appears that polymorphism is an even more common phenomenon among organic than among inorganic compounds in the temperature range of this work, solid  $\text{CO}_2$  temperature to  $200^\circ$ . This might be expected, because it has appeared that the chance that a substance will exhibit polymorphism is roughly greater the lower the melting point, and in general the melting points of organic substances are lower than those of inorganics. To compensate for the greater frequency of polymorphism with organics is the fact that the transitions are generally more sluggish and with smaller volume changes, so that they are much more difficult to measure experimentally, it results that they are of less interest. In fact, a number of cases will appear in the following in which I have not thought it worth while to take the great trouble that would be necessary to determine satisfactorily all the transition parameters, but have let the matter rest with a rather superficial statement of the existence of the transition and its order of magnitude.

The scheme of selecting the compounds for examination in the following was simple. In the absence of any theory, polymorphism may be expected to be incident anywhere. The most significant cases are, in general, those occurring among the substances with simplest structure. After measuring a few common compounds in the Laboratory stock, I adopted the scheme of selecting from the list of organics in International Critical Tables those of the lowest molecular weight, and therefore simplest structurally, which were readily procurable commercially. Unless the contrary is stated, all the compounds used in the following were obtained from the Eastman Kodak Co., and were of their purest grade.

In addition to the measurements with the regular volume apparatus, the shearing phenomena of a number of the substances were investigated as an auxiliary method of exploring for the presence of polymorphism<sup>1</sup>. These shearing phenomena have a certain intrinsic interest of their own, and since it is hardly worth while to write a separate paper describing them, some account will also be given in the following of the results of the shearing measurements. In general characterization, the shearing phenomena of organic substances differ from those of inorganic substances in the much more rapid rise with pressure of the shearing strength of the former. The rise is often linear with pressure, and even often more rapid than linear, so that the curve of shearing strength is concave upward, whereas for

inorganic substances the curve is almost always concave downwards. Initially, organic substances are weak in shear, as is to be expected, but with increasing pressure the strength rapidly increases, and at the maximum pressure of 50,000 the strength averages about that of the usual inorganic compound. There are not, however, any cases of extreme strength corresponding to some of the exceptionally strong inorganic substances, and in general the range of shearing strength in organic substances under high pressure is much narrower than that of inorganics. The rapid increase of shearing strength of organics under pressure reminds one of the very great increase of viscosity of organic liquids under pressure. The mechanism of the two phenomena may well be related, involving an interlocking effect between molecules of complicated shapes.

In the following the shearing measurements on those substances which exhibit polymorphism or which have been explored for polymorphism with negative results are described in connection with the discussion of the phenomena of polymorphism. In addition, the shearing phenomena have been investigated for a number of substances which have not been explored for polymorphism in the volume apparatus, these are described in a separate section.

The presentation of detailed data now follows.

#### DETAILED DATA

*Carbon Tetra bromide* The phase diagram of this substance has been already investigated.<sup>2</sup> There is a transition at atmospheric pressure at 47°, and there is a third form at higher pressures. In this work an additional form was found at pressures above 10,000, making four modifications in all. Runs were made with two different set-ups of the 50,000 apparatus, at temperatures from room temperature to 175°, eight runs in all.

At temperatures below 130°, the dynamics of this transition are unique, there being an enormous asymmetry. On increasing pressure at temperatures below 130° the transition does not run even up to nearly 50,000, but on releasing pressure the transition runs, irreversibly of course, and with *decreasing* volume. This is highly paradoxical, and at first seems contrary to thermodynamics, that is, a transition with decrease of volume brought about by a decrease of pressure. There is, however, no violation of thermodynamics, the transition being irreversible. The phenomenon is doubtless connected in some way with nucleus formation. Nucleus formation takes time, on the first increase of pressure there was not time for sufficient for-

mation of nuclei, and it was only after release of pressure that sufficient time had been spent in the critical region of nucleus formation to permit the formation of enough nuclei to make possible the transition. In nearly all the experiments the application and release of pressure was done on a careful time schedule, 1,000 kg/cm<sup>2</sup> per minute. The pressure at which the irreversible transition runs with decrease of pressure becomes higher the higher the temperature. This is as would be expected, because at higher temperatures nucleus formation is easier, so that not so long a sojourn in the critical region is necessary, and a higher pressure means a shorter sojourn. At room temperature, the pressure at which the irreversible transition would run on release of pressure has dropped below the reversible transition line, and the transition does not run at all, up to 50,000 and back. At 150° and higher, the speed of nucleus formation has become sufficiently great so that the transition runs irreversibly, with volume decrease as normal, on the first increase of pressure. At 173° the velocity of nucleus formation has increased further, and now the super-pressure required is very much reduced.

Figure 1 shows the phase diagram, and indicates the points at which the transition runs. The points obtained with the two different set-ups are rather consistent. This might not be expected of a thing as capricious as these inhibition phenomena usually are, and indicates that the results have a certain significance.

The reverse transition, from IV to II apparently runs normally enough. It is obvious that the location of the reversible transition line is in great doubt when the limits of indifference are as wide as they are here. I have drawn it with the same general slope as that of the line connecting the points marking the lower pressure of indifference, but this is evidently arbitrary, and in fact it can be argued that the line should be steeper than drawn, since usually the limits of indifference become wider at lower temperatures.

It is hardly worth while giving a table for the transition parameters. The slope of the transition line is in such great doubt that no significance can be attached to any estimated latent heat. The change of volume is small and scattering, the extreme values being 0.004 and 0.009 cm<sup>3</sup>/gm. A mean value for  $\Delta V$  is 0.0075 cm<sup>3</sup>/gm. There is no evidence for any significant variation of  $\Delta V$  with temperature.

A further study of the phenomena of nucleus formation would probably be of interest. I made one set of measurements that shows that the phenomena are not simple. At 100° pressure was increased to 50,000 without the transition running; then on decrease of pressure

the transition ran irreversibly with volume decrease at 23,500, and then on further decrease ran in the opposite direction at 8,300. All this was on the regular time schedule, and was in duplication of the first run, and consistent with it. Pressure was now raised to 23,000,

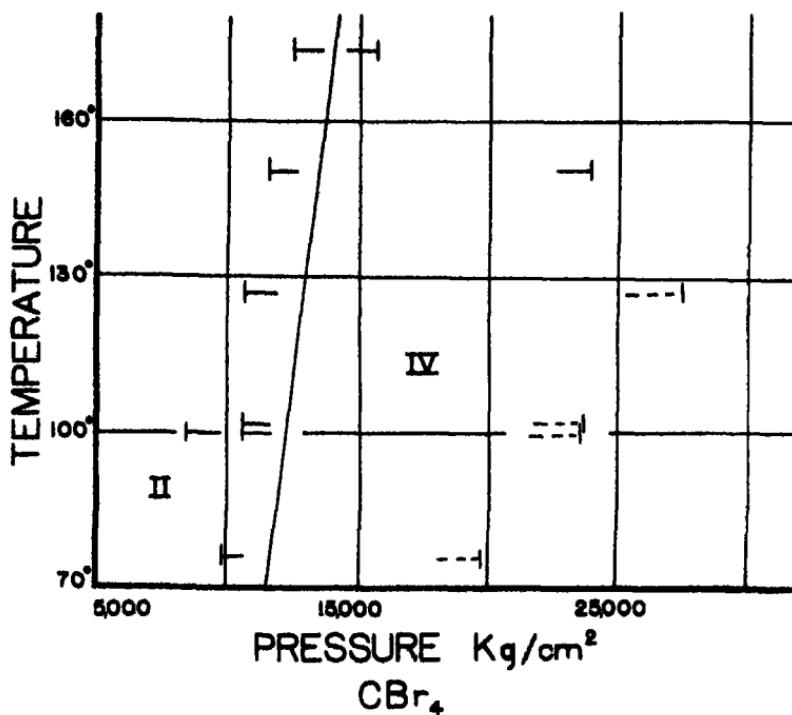


FIGURE 1. The transition pressures of the new high pressure modification of  $\text{CBr}_4$  as a function of temperature. The dotted lines indicate that the transition ran with decreasing pressure after an excursion to 50,000. The transitions of II with I and III occur at pressures below 5,000, and have been studied previously.

14,000 beyond the reversible transition point, and left over night, temperature being maintained at 100°. No transition took place over night. This was a great surprise, since I thought that the rate of nucleus formation at 23,000 would be sufficiently great to start the transition in a time approximately 15 times as long as before. In the morning pressure was increased from 23,000 on the regular time schedule, 1,000 kg per minute up to 40,000, with no transition, then

released back to 14,000 (9,000 beyond the place where the transition had taken place on the first release) with no transition, and then back, the transition now starting and running to completion at 24,300 with increasing pressure

$\text{CBr}_4$  is known to decompose appreciably at its melting point at atmospheric pressure at about  $90^\circ$ , and in my former work decomposition was very troublesome. It was apparently complete at  $175^\circ$  and pressures below 7,000. In this work no trace of decomposition was found after the run at  $175^\circ$ . Again we have evidence that pressure is effective in preventing a decomposition that proceeds with increase of volume.

The shearing curve has a marked downward break at room temperature at  $15,000 \text{ kg/cm}^2$  corresponding to the transition above. The high pressure modification thus has a lower shearing strength than the low pressure modification, a somewhat unusual fact. The shearing curve of the high pressure modification rises with general concavity toward the pressure axis. The shearing strength reaches  $2,300 \text{ kg/cm}^2$  at a pressure of  $50,000 \text{ kg/cm}^2$ .

*Iodoform* Three runs were made with this substance the seasoning run at room temperature, one at  $50^\circ$ , and one at  $150^\circ$ . There appear to be three small but quite definite transitions. These could be established with greater certainty with increasing than with decreasing pressure, either an asymmetry in the transition or the greater curvature of the isotherm obscuring the effect with decreasing pressure. The lower transition, however, was picked up fairly certainly with decreasing pressure at  $150^\circ$ . The equilibrium lines are shown in Figure 2. Since the transition pressure was not established with decreasing pressure, except for the point mentioned, there is obviously no basis for an estimate of the most probable direction of the transition lines, which are schematically indicated by the dotted lines.

The change of volume at the transition I-II is of the order of  $0.0002 \text{ cm}^3/\text{gm}$ , that of the other transitions is perhaps one half as much. There is no point in attempting to calculate the transition parameters.

The shearing curve has a gentle upward inflection in the neighborhood of 30,000, doubtless the transition at highest pressure of those found above brought down to room temperature. The shearing curve of the high pressure modification is concave upward, whereas below the transition the curve is concave downward. The shearing strength at 50,000 is  $2,800 \text{ kg/cm}^2$ .

*Cyanamide* Two runs were made the seasoning run at room temperature, and a run at  $125^\circ$ . There appears to be a very small transi-

tion at  $125^\circ$ , at  $25,300 \text{ kg/cm}^2$ , and with a volume change of the order of  $0.0003 \text{ cm}^3/\text{gm}$

*Urea (Carbamide)* Runs were made with a single filling of the apparatus at room temperature,  $80^\circ$ ,  $90^\circ$ ,  $150^\circ$ , and  $200^\circ$ . This material has already been found to have two high pressure modifications.<sup>3</sup> The transition line between I and III runs from  $4,300$  at  $0^\circ$  to  $6,750$  at  $102.3^\circ$ , the triple point, and the line I-II from the triple point to  $7,070$  at  $160^\circ$ . With the present set-up, these transitions

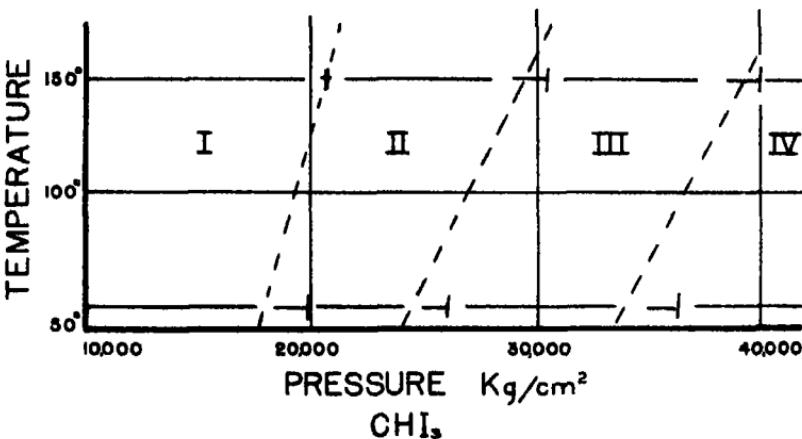


FIGURE 2 The transition pressures of  $\text{CHI}_2$  as a function of temperature. The transitions are highly unsymmetrical, occurring with practical speed only with increasing pressure, so that the true location of the transition lines is in much doubt

were located in practically the positions given, but no attempt was made to repeat the measurements of the parameters. In addition, the existence of at least three new high pressure forms was established with great probability. The volume changes of these are small, however,  $0.007 \text{ cm}^3/\text{gm}$  at the most, and since the transitions are sluggish and not easy to measure, I did not try for accurate values of the parameters. At  $80^\circ$  and  $90^\circ$  two transitions were found, the first running between  $10,000$  and  $11,000$ , and the second at approximately  $20,000$  at  $80^\circ$  and  $19,000$  at  $90^\circ$ . At  $150^\circ$  there is probably another transition at approximately  $25,000$ .

At atmospheric pressure urea decomposes with very appreciable velocity at the melting point near  $130^\circ$ . It has been my previous experience that decomposition can often be prevented by the applica-

tion of high pressure. After the exploring run at  $150^{\circ}$ , temperature was raised to  $200^{\circ}$  and pressure to approximately 30,000. Pressure was kept here for one hour, and then the apparatus was allowed to cool over night without release of pressure. On opening the apparatus in the morning, no evidence of decomposition could be found. It would seem that there might be interesting possibilities here in the

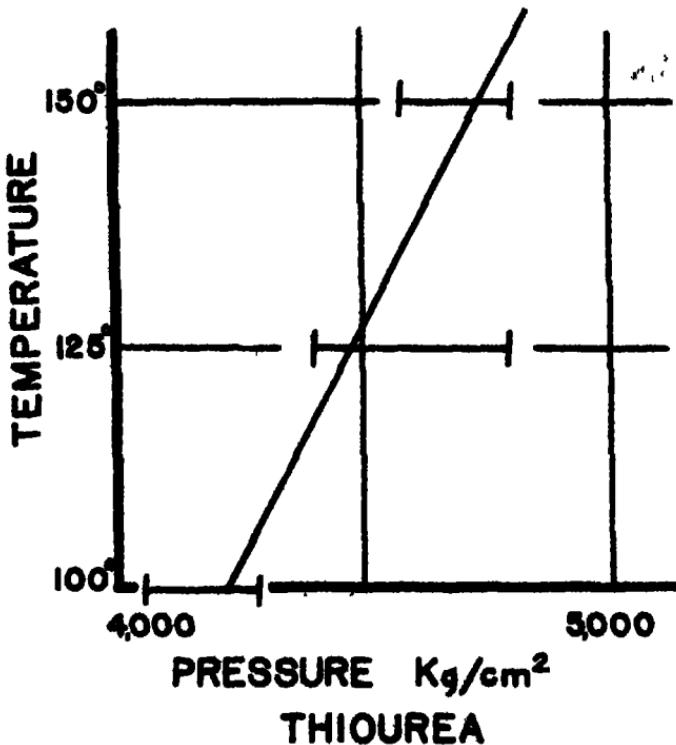


FIGURE 3 The transition pressures of thiourea as a function of temperature

way of producing new reactions at high pressures between organic compounds at temperatures so high that under normal conditions there would be decomposition.

Very rough values for compressibility could be obtained from the piston displacements  $\Delta V$  in  $\text{cm}^3/\text{gm}$  was 0.06 between 10,000 and 30,000, and 0.09 between 10,000 and 50,000.

The shearing curve of urea has a very definite abnormality between 22,000 and 28,000. Up to 22,000 the shearing curve is nearly linear

At 22,000 there is an upward break in direction, but the curve between 22,000 and 28,000 is distinctly concave downward. At 28,000 there is another upward break in direction, less pronounced than that at

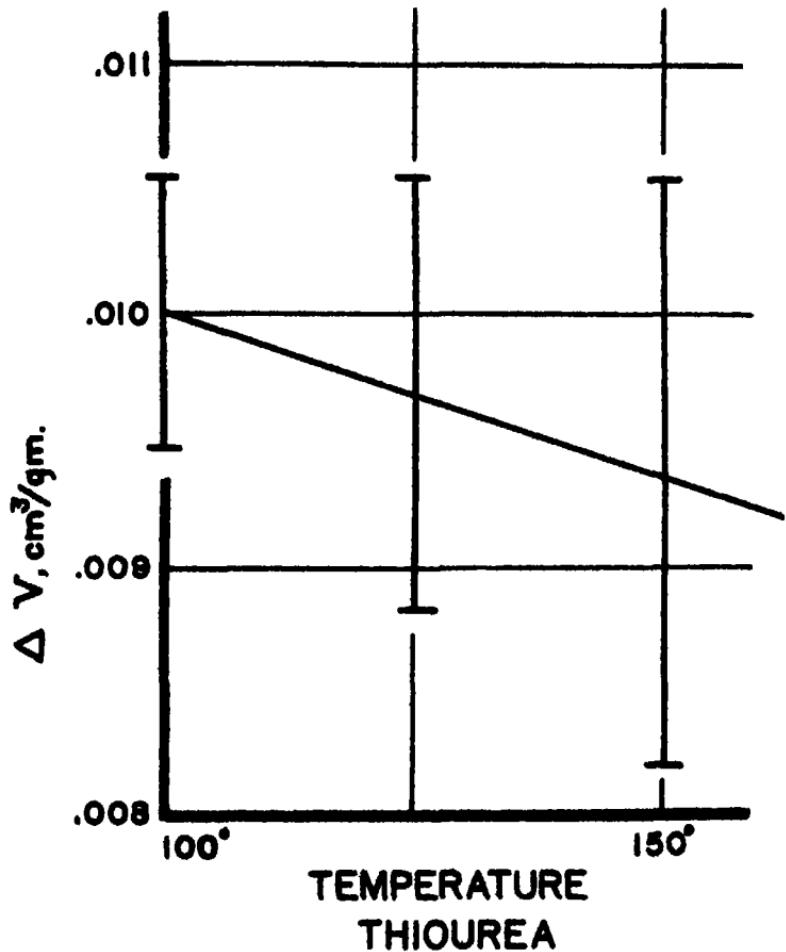


FIGURE 4 The volume changes of thiourea as a function of temperature

22,000 and beyond 28,000 the curve is nearly linear with a tendency to upward curvature. The abnormality is doubtless due to the two transitions mentioned above, at 20,000 and 25,000, brought down to room temperature and imperfectly resolved. The shearing strength at 50,000 is 2,900 kg/cm<sup>2</sup>.

*Thiourea* Runs were made with the small and the large apparatus. With the small cylinder exploration was made out to 50,000 at room temperature and 125°. At 125° a transition was found at such low pressures that it was necessary to set up in the larger cylinder in order to get more accurate values. With this apparatus runs were made at 100°, 125°, and 150°.

The phase diagram is shown in Figure 3, the changes of volume in Figure 4, and the transition parameters in Table I.

TABLE I  
TRANSITION PARAMETERS OF THIOUREA

Pressure kg/cm <sup>2</sup>	Temperature 100°	$\frac{dr}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
4,230	100°	0980	0100 <sub>4</sub>	38 1	893
4,740	150°	0980	0093 <sub>4</sub>	40 3	945

The shearing curve of thiourea is more concave than usual toward the pressure axis up to 25,000, where there is a flat inflection, with upward concavity beyond this up to 50,000. The shearing strength at 50,000 is 4,000, higher than that of most organic substances. The point of inflection has been the accompaniment of transitions established in the volume apparatus in a number of other cases, but no evidence for it could be found here. One suspects a transition with very small volume change.

*Ammonium Thiocyanate* Two set-ups were made. The first, with the regular high pressure apparatus, showed the existence of a transition at very low pressures at room temperatures, and nothing else up to nearly 50,000, and at 125° nothing up to about 45,000. A second set-up was accordingly made with the 3/8 inch apparatus to get more accurate values. Runs were made with this at 0°, room temperature, 51°, and 75°. There is an ice-type transition, with a transition at atmospheric pressure which extrapolates to a temperature of 88°. The volume change is fairly large and runs cleanly, so that fairly good values could be obtained at the two lower temperatures where the pressures are higher. At the two higher temperatures, however, the pressures are so low that accurate values could not be obtained, and in fact the whole range of the phenomenon is at such low pressures as to make it poorly adapted for the present apparatus. The approximate transition parameters are given in Table II. It should be easy to considerably improve on the accuracy of these values if one wanted to construct special apparatus. Instead of giving diagrams as usual,

I have shown the experimental data in the bottom part of Table II. It will be seen on plotting that the experimental points for pressure and temperature lie very smoothly. It is therefore probable that the very distinct upward curvature of the transition line is genuine.

*Nitro-guanidine.* Runs were made to the maximum pressure at room temperature and 150°. At room temperature evidence of a sluggish transition with small change of volume was found with decreasing pressure at 40,000. This was found both on the seasoning run and on two subsequent repetitions.

TABLE II  
TRANSITION PARAMETERS OF AMMONIUM THIOCYANATE

Pressure kg/cm <sup>2</sup>	Temperature °	$\frac{dr}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
0	88°	040	0419	378	8.9
1,000	53°	031	0412	433	10.2
2,000	26	024	0407	507	12.0
3,000	5°	018	0402	622	14.7

#### EXPERIMENTAL DATA

3,310	0°	{	0411
			0392
2,130	23°	{	0416
			0396
1,080	51	—	—
2,130	74°	—	—

At 150°, the results were complicated. Readings were obtained normally enough starting at low pressures. At 10,000 there was apparently a rapidly running transition, which ran to completion in four minutes, with volume change of 0.0095 cm<sup>3</sup>/gm. At 22,000 there was another volume discontinuity of 0.0027 cm<sup>3</sup>/gm, which ran to completion in two minutes. Again at 29,000 there was a smaller volume discontinuity of 0.0018 cm<sup>3</sup>/gm, running to completion in 2 minutes. There was nothing more up to the maximum. On release of pressure, a small discontinuity was found at 38,000, evidently the same thing that had been found before at room temperature. What was probably the transition at 29,000 was next picked up, but this did not run as sharply as with increasing pressure, but the transition was spread over a pressure interval of 4,000 kg and a time interval of 6 minutes. The next transition which should have been picked up was that at 22,000, but it started at a pressure somewhat above 22,000,

and ran for 90 minutes before being completed, and with a volume change of  $0.014 \text{ cm}^3/\text{gm}$ , against  $0.0027$  found with increasing pressure

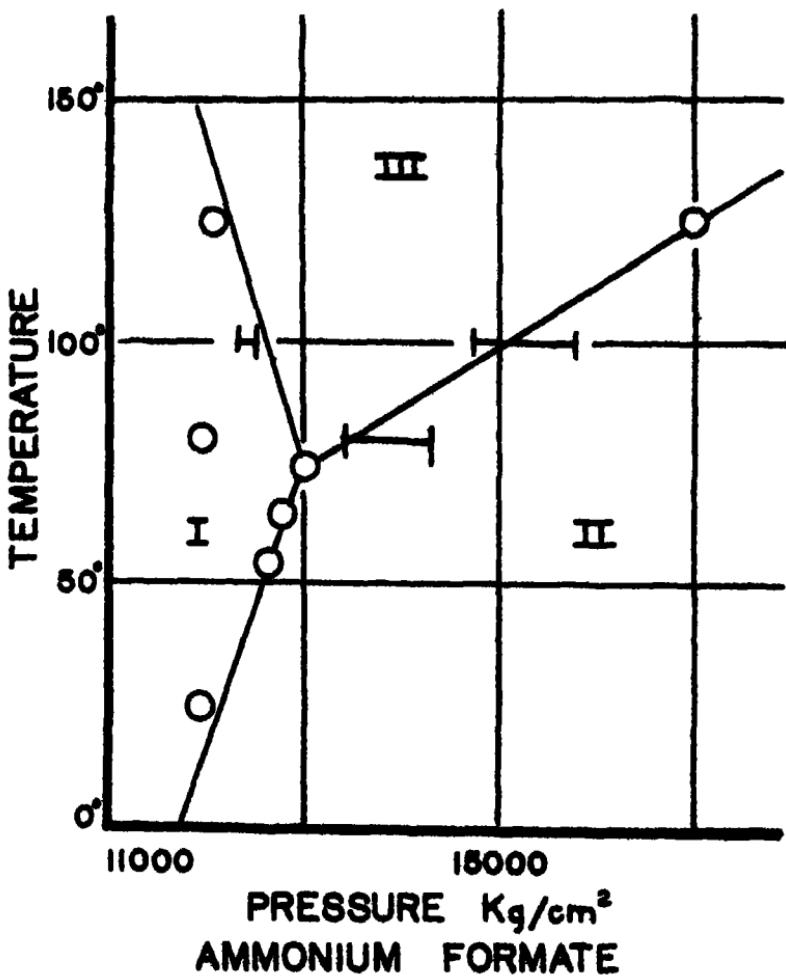


FIGURE 5 The transition pressures of ammonium formate as a function of temperature

From here on the curve with decreasing pressure was entirely different from that with increasing pressure, the material expanded abnormally rapidly, indicating too great a volume, and already at 6,500 had

reached the initial volume on the first increase. There was no trace of the lowest transition at 10,000. On taking the apparatus apart there was a strong NH<sub>3</sub> smell, and there was blue discoloration of the copper washers. Evidently the material had decomposed in the neighborhood of 25,000. Decomposition must have been complete here, because the subsequent readings showed no creep. The volume change 0.014 represents the difference of volume at 25,000 between the original material and the decomposition products. At atmospheric

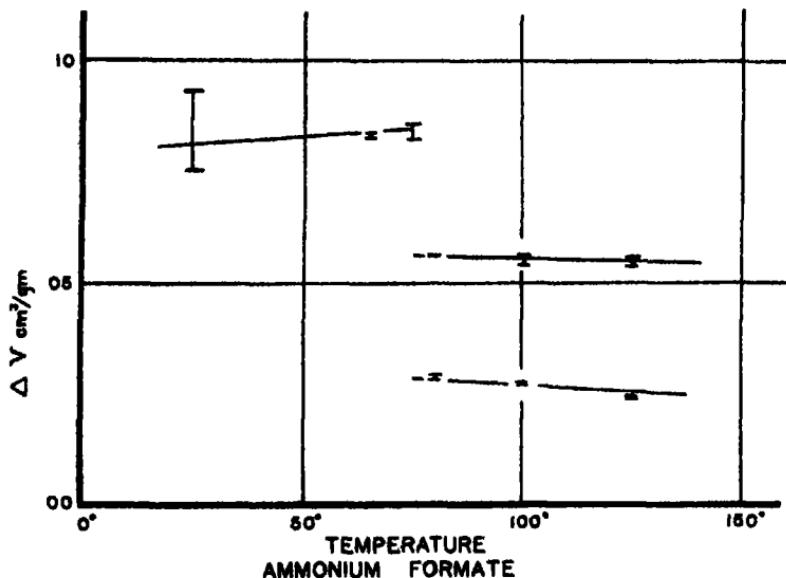


FIGURE 6 The volume changes of ammonium formate as a function of temperature

pressure the volume difference is much larger, which means that the decomposition products are much more compressible than the initial material.

The puzzle is to understand why the material did not decompose on the initial application of pressure.

*Ammonium Formate* Two set-ups were used. The first was with the 0.265 inch apparatus, and with this five runs were made, from room temperature to 150°. The run at 150° was terminated by leak. These runs established the existence of three modifications, and gave fairly accurate values both for the transition pressures and the change of volume. The transitions run cleanly, with large volume change.

No other modifications were found out to the maximum at room temperature or  $125^{\circ}$ . The second set-up with the more sensitive apparatus was made in order to obtain more data from which the triple point could be located more closely. Runs were made at  $80^{\circ}$ ,  $100^{\circ}$ ,  $65^{\circ}$ , and  $55^{\circ}$  with the second set-up.

The phase diagram is shown in Figure 5 and the changes of volume in Figure 6. The transition parameters are sufficiently characterized by their values at the triple point, which are given herewith. The equilibrium lines in Figures 5 and 6 were adjusted so as to satisfy the additive relations at the triple point.

TABLE III

## TRANSITION PARAMETERS OF AMMONIUM FORMATE AT THE TRIPLE POINT

Pressure kg/cm <sup>2</sup>	Temper- ture	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
		I-II      0577	0850	505	21 6
13,000	75°	I-III    - 0674	0562	-287	-12 2
		III II    0125	0288	792	33 8

*Urea Nitrate* Runs were made to the maximum at room temperature (seasoning run and regular run) and at  $150^{\circ}$ . At room temperature nothing was found. At  $150^{\circ}$  a very small, but apparently real transition, was found at 24,000. Consistent values for the equilibrium pressure were obtained with both increasing and decreasing pressure, and also consistent values for the change of volume, namely  $0.0002 \text{ cm}^3/\text{gm}$ . The transition ran to completion in two minutes.

On further release of pressure, decomposition with large increase of volume began at about 5,000, and continued, automatically increasing the pressure to at least 9,000. Here the temperature was reduced. On opening the apparatus, there was evolution of gas. Decomposition did not occur on the initial application of pressure, because the initial pressure at  $150^{\circ}$  was chosen as 12,000, with the specific purpose of preventing the anticipated decomposition.

In view of the smallness of the transition it did not seem worth while to set the apparatus up again for further measurement.

*Methylamine Hydrochloride* Six runs were made with a single set-up at temperatures from room temperature to  $175^{\circ}$ .

The phase diagram is complicated, with five modifications. In general, this is one of the easier substances to investigate, the volume changes are fairly large, and the transitions run rather easily, without particularly wide region of indifference or great sluggishness. Only

one transition failed to run sharply enough to make the interpretation of the results secure, namely the transition V-III just above the triple point. However, the location of the transition lines demanded by the other points seemed so unequivocal that I believe there can be no question of the general character of the relations of the phases.

The phase diagram is shown in Figure 7, the changes of volume in

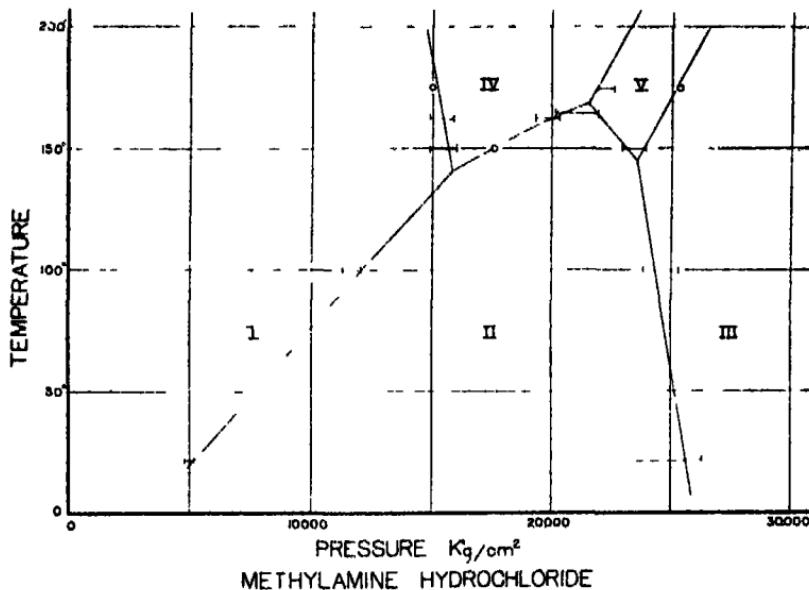


FIGURE 7 The transition pressures of methylamine hydrochloride at different temperatures

Figure 8, and the transition parameters at the three triple points in Table IV. The location of the transition lines and the magnitudes of the changes of volume have been so adjusted that the additive relations are satisfied at the triple points. It has been possible to do this without doing any serious violence to the experimental points, as the diagrams show. It would probably be possible to make a somewhat better adjustment, for instance drawing the line I-II with normal curvature, in such a way that it would pass between the extreme points at 100°, but any changes which would be made in this way are so slight that it seemed hardly worth while. I do not, as usual, give a table of the transition parameters at various points on the transition lines, it should be possible to get accurate enough values of these

if necessary from the diagrams and the parameters at the triple points

The rapid variation of volume on the line IV-II is the only particularly unusual feature shown by this substance

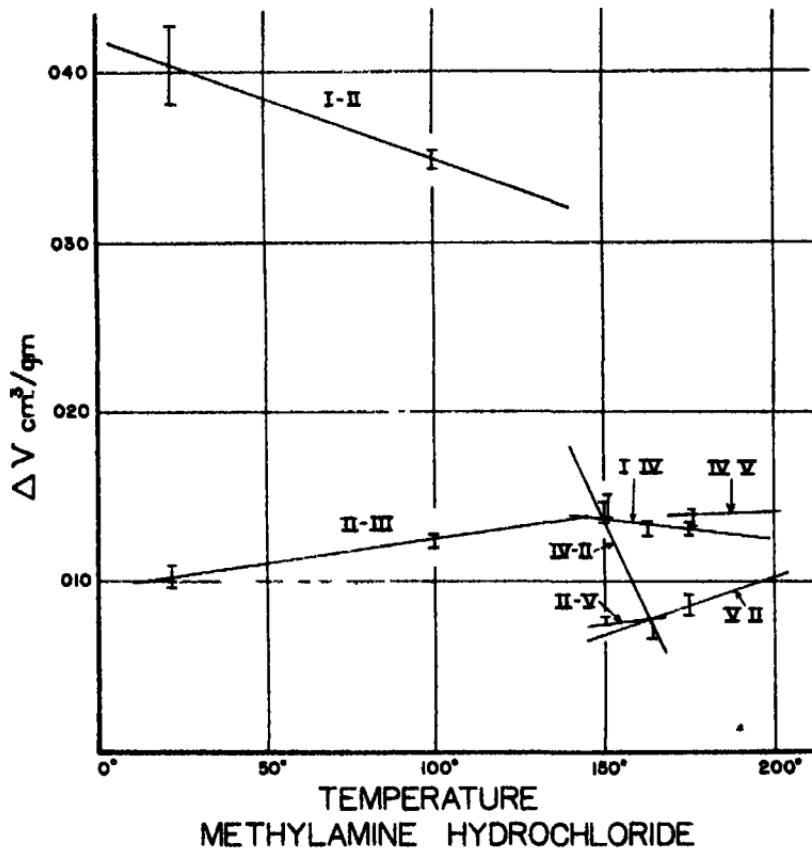


FIGURE 8 The volume changes of methylamine hydrochloride as a function of temperature

*Semi-carbazide Hydrochloride* Two different set-ups were used with this substance, with the first there were five runs at temperatures from room temperature to 150°, and with the second three, from room temperature to 142°.

There is a fairly large transition at low pressures. The transition is

unusual in that the band of indifference is wide, and the width does not fall off noticeably with increasing temperature, while on the other hand, when the transition once starts it runs sharply to completion with no further change of pressure. The runs did not entirely clean up the nature of the behavior at 140° and 150°, but there were anomalies which may or may not be real, the interpretation being obscured by difficulties with the apparatus of one sort and another on the first run, and rupture of the cylinder on the second, together with possible decomposition. On the last run at 142°, a transition was found with

TABLE IV  
TRANSITION PARAMETERS OF METHYLAMINE HYDROCHLORIDE  
AT TRIPLE POINTS

Phases	Pressure kg/cm <sup>2</sup>	Temperature Centigrade	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm gm cal/gm
I-II-IV	15,800	140	I-II	01100	0320 -1200 -28 1
			I-IV	-058	0140 100 2 3
			IV-II	00570	0180 -1300 -30 4
II-IV V	21,500	168°	IV-V	0175	0140 -354 -8 3
			IV-II	0040	0060 -662 -15 5
			II-V	-0115	0080 308 7 2
II-III-V	23,500	145°	II-IV	-0580	0140 101 2 35
			II-V	-0115	0074 209 5 05
			V-III	0175	0086 -158 -2 70

increasing pressure at 11,000 (higher than would be expected from the results at lower temperatures) and with a volume change only one fifth that to be expected. The run was terminated by rupture, and a certain interpretation does not appear.

At 75°, 100°, and 125° the transition pressures found with increasing and decreasing pressure were respectively 8,200 and 2,300, 8,800 and 2,100, and 9,800 and 2,100. The corresponding changes of volume were 0.0198 and 0.0211 cm<sup>3</sup>/gm, 0.0185 and 0.0218; and 0.0178 and 0.0217. Probably the best mean result is a transition pressure of 5,500 kg/cm<sup>2</sup> and a change of volume of 0.020 cm<sup>3</sup>/gm, both independent of temperature.

*Dichloro-acetamide*. Four runs were made with this one at room temperature to 50,000, one at 75°, and two at 125°. There is a transition, with fairly large change of volume, in the general neighborhood of 10,000. In spite of the fact that  $\Delta V$  is large, good values were not

obtained for the transition parameters. At room temperature it appeared as if there were two transitions, an upper one at 13,500 and a

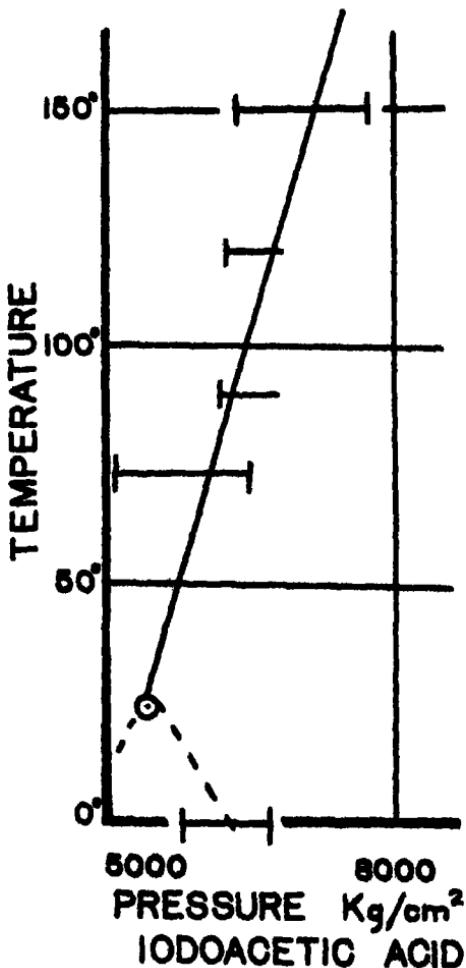


FIGURE 9 The transition pressures and temperatures of iodoacetic acid. It is probable, but not certain, that the transition line forks at the lower end lower one at 9,500. At 75°, only a single transition was found, at 7,100. At 125°, the two runs gave for the transition pressure 8,900 and 10,600. The region of indifference was imperceptibly narrow at

all temperatures; the pressures given are means from above and below. The pressures just given do not fit into a sensible phase diagram unless there is abnormally great curvature of the transition lines.

The changes of volume, although fairly large, were difficult to measure because the transition runs at low pressures where the curvature is so great that frictional lag makes an unusually large error.

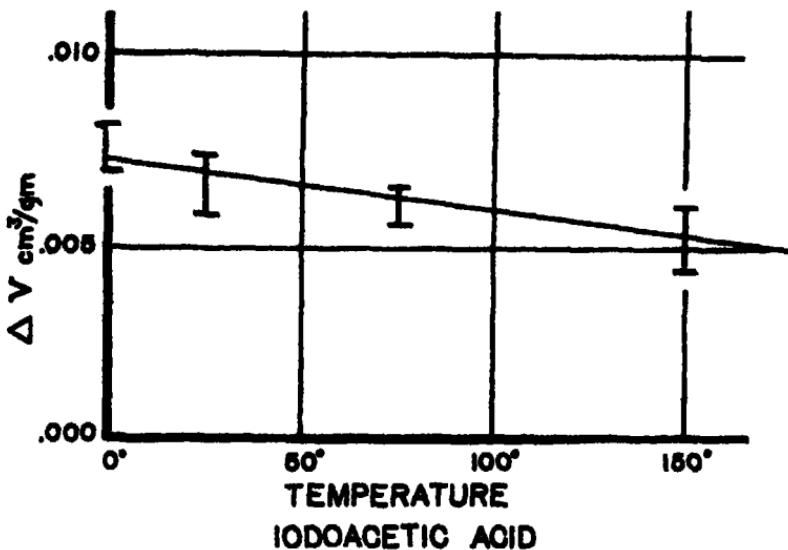


FIGURE 10 The volume changes of iodoacetic acid as a function of temperature

The values for  $\Delta V$  varied capriciously between 0.030 and 0.042 cm³/gm, 0.038 is probably a representative average. In view of the irregularity of the results I do not give a diagram or table of the results.

*Iodoacetic Acid* Seven runs were made with a single set-up, the seasoning run and a measuring run at room temperature, and runs at 0°, 75°, 150°, 120°, and 90°. There was leak on the last two runs, so that these runs did not give values for  $\Delta V$ , and only the equilibrium pressure with decreasing pressure

There is a transition at low pressures—between 5,000 and 7,000. The equilibrium diagram is shown in Figure 9, the change of volume in Figure 10, and the transition parameters in Table V. It is highly

probable that the transition line forks at the lower end, below room temperature. This is suggested both by the location of the transition point at 0°, lying off the curve with the others, and the fact that at room temperature there was no appreciable width to the band of indifference. This latter is characteristic of the behavior just below a triple point. The possible fork in the transition line is indicated by the dotted lines in Figure 9. It would have been difficult to establish this suspected low temperature transition with certainty because of the sluggishness of the reaction.

*Oxamide.* With the original set-up the usual seasoning run was made at room temperature, and runs at 100°, 125°, 150°, and 175°. The appearance was that of a most complicated phase diagram, with perhaps a half dozen transitions, none with volume change more than 0.0010 cm<sup>3</sup>/gm, spread through the range from 15,000 to 45,000.

TABLE V  
TRANSITION PARAMETERS OF IODOACETIC ACID

Pressure kg/cm <sup>2</sup>	Temperature Centigrade	$\frac{dr}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Heat gm cal/gm
5,100	0°	0.715	0.072	27.5	0.65
5,800	50°	0.715	0.066	29.9	0.70
6,500	100°	0.715	0.059	30.8	0.72
7,200	150°	0.715	0.053	31.4	0.73

Nine months later two new set-ups were made with runs at 125°, 175° and 200°. Small irregularities were again found, the more prominent of which were definitely repeatable with different set-ups. The most prominent is in the neighborhood of 20,000. It is highly probable that there are a number of transitions so small as to be on the margin of what can be detected with the present apparatus. In view of the complication and difficulty I did not think it worth while to try for more definite results.

At the termination of each of the two repetitions of the experiment it was noticed that the residue had a sweetish odor, distinctly unlike that of the original material. Some chemical transformation is therefore suggested. There was, however, no evidence of gaseous decomposition.

The shearing curve is at first concave downward, then there is a flat inflection near 10,000, upward concavity for a short distance, a second flat inflection near 18,000, then downward concavity with a third flat inflection near 30,000, followed by upward concavity, to a

shearing strength of 4,000 kg/cm<sup>2</sup> at 50,000. The shearing curve therefore bears out the evidence of the other apparatus for a number of obscure transitions.

*Acetamide* This substance is already known to have a transition,<sup>4</sup> the line running from 6,000 at 20° nearly vertically to 5,390 at 127°, the triple point with the liquid. Eight runs were made with the 50,000 apparatus between room temperature and 200°, and with the 3/8 inch

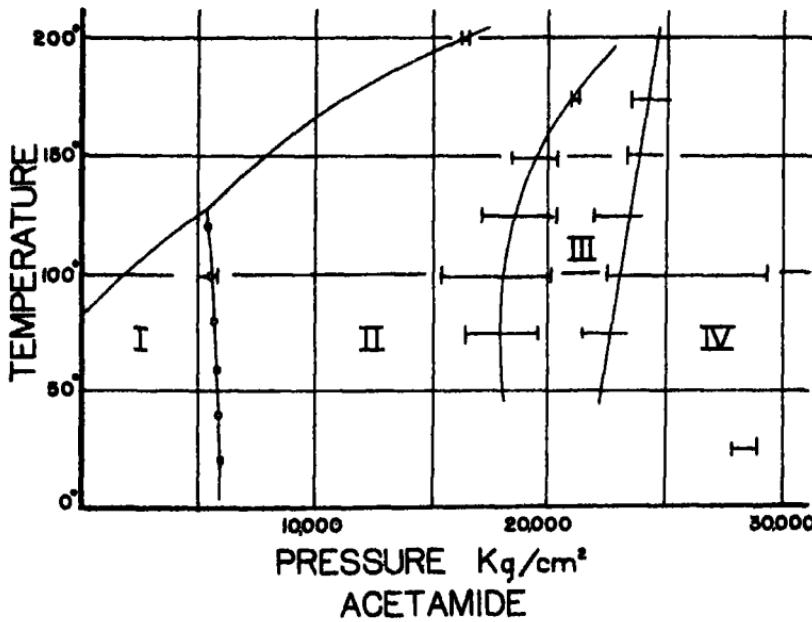


FIGURE 11 The transition pressures and temperatures of acetamide. The circles indicate the previously determined data. Note the isolated transition at 25° near 30,000, between two totally unstable forms.

piston apparatus, a couple of runs at room temperature and 175°. Two new stable forms were found at high pressures, making four stable forms in all. In addition, it is reported in the literature that acetamide readily crystallizes from the melt in an unstable modification. I did not find this unstable form in my previous work, but in the present work, the form initially obtained from the melt and with which the first run was made at room temperature must have been this unstable form. This unstable form experiences a reversible transition to what is in all probability still another modification.

This reversible transition of the unstable form was found twice, first on the seasoning application of pressure, and then on the second application, when the coordinates were measured more carefully. It occurs between 27,800 and 28,900 kg/cm<sup>2</sup>, and the values found for  $\Delta V$  with increasing and decreasing pressure were 0.0031 and 0.0027 cm<sup>3</sup>/gm. On the second release of pressure the unstable form was

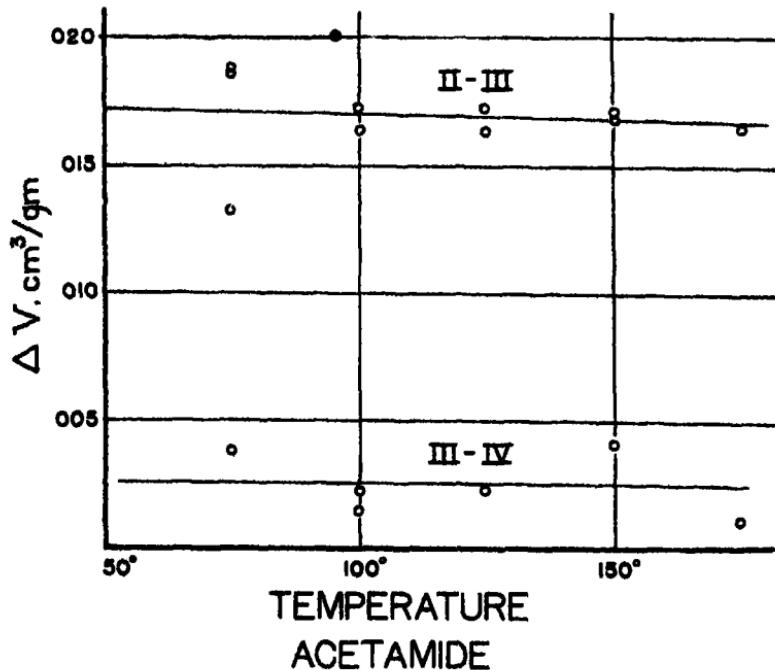


FIGURE 12 The volume changes of acetamide as a function of temperature

apparently irreversibly replaced by the stable form between 7,500 and 5,000 with a volume increase of 0.0215 cm<sup>3</sup>/gm. The conditions of appearance and disappearance of the unstable form are of course capricious. With the second set-up, with the 3/8 inch piston, the initial material was also the unstable form. At room temperature, pressure was increased to 25,000, released to 0 and increased to 12,000 without the transition running. On raising temperature at 12,000, the unstable form irreversibly transformed into II, with decrease of volume. The volume of the unstable form at pressures above 5,000 is thus intermediate between that of I and II. The location of the

various transitions makes it certain that the unstable form at atmospheric pressure is not the high pressure modification II. The unstable form measured at atmospheric pressure by Körber<sup>6</sup> is less dense than I. If my unstable form is the same as that of Körber, its compressibility must be very materially larger than that of I.

The principal interest, of course, is in the reversible transitions of the stable forms. The phase diagram is shown in Figure 11 and the changes of volume in Figure 12, and the parameters of the transitions in Table VI. In addition to the points on the two new lines II-III

TABLE VI  
TRANSITION PARAMETERS OF ACETAMIDE

Pressure kg/cm <sup>2</sup>	Temperature Centigrade	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat	
II-III					
18,000	80°	∞	0172	0	0
18,100	100	083	0170	77	1 8
19,500	150	0217	0168	330	7 7
23,000	200	0100	0166	790	18 4
III-IV					
22,200	50	0625	0025	13	30
23,000	100	0625	0025	15	35
23,800	150	0625	0025	17	39
24,600	200	0625	0025	19	44

and III-IV, a check point was obtained on the line I-II at 100°, giving a transition pressure below 5,800 and a  $\Delta V'$  of 0.0315 cm<sup>3</sup>/gm, against the equilibrium value 5,590 and  $\Delta V'$  of 0.0321, found formerly. The check is as good as could be expected. In addition, a point was inadvertently obtained on the melting curve at 200°. Good values for the equilibrium pressure were obtained, 16,500 and 16,200 from above and below, but  $\Delta V$  could not be obtained because of leak, and in fact the experiment had to be discontinued at this point because of leak of the liquid.

The transition III-IV is unusual in that no good values of either the equilibrium pressure or of  $\Delta V$  could be obtained with increasing pressure. Unusually great super-pressure is needed to start the transition, and even when started it runs very sluggishly. In order to ensure completion of the transition, pressure was usually carried up nearly to the maximum. On decreasing pressure, however, the state of affairs is quite unsymmetrical, the transition running easily, with

sharp  $\Delta V$ . The exact location of the thermodynamic transition line (that is, the line on which the thermodynamic potentials of the two phases are equal) must be in doubt, in the diagram I have drawn it rather near the lower pressure limit. The line II-III is unusual because of its marked curvature. An alternative explanation would be that the line forks at the lower end, with still another modification, and I cannot claim that this possibility is excluded. However, no trace

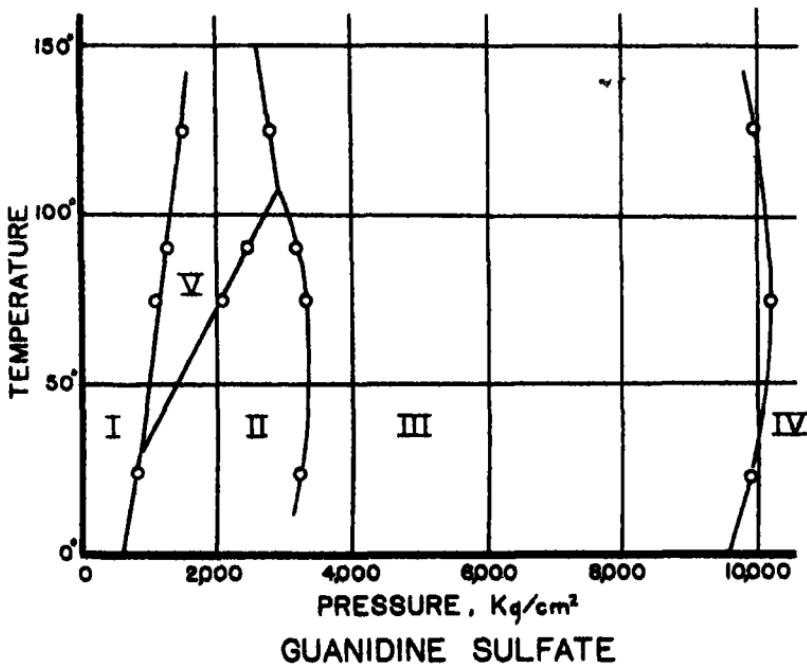


FIGURE 13 The transition pressures and temperatures of guanidine sulfate

of a new transition line below  $80^\circ$  was found, and the volume relations are not favorable. If there is another transition, it must run with very small change of volume.

Modification IV is distinctly more compressible than III, in spite of its smaller volume. This is the usual relation.

The shearing curve of acetamide has a sharp downward break (high pressure form with lower strength) at about 20,000, where the strength is  $2,000 \text{ kg/cm}^2$ . Below and above the break the curve is linear, rising to a strength of  $3,600$  at  $50,000 \text{ kg/cm}^2$ . There can be

little question but that the break is the combination of transitions II-III and III-IV carried down to room temperature and unresolved, because of their closeness.

*Guanidinium Sulfate* Runs were made with three different set-ups. Two of these were with the regular high pressure apparatus at room

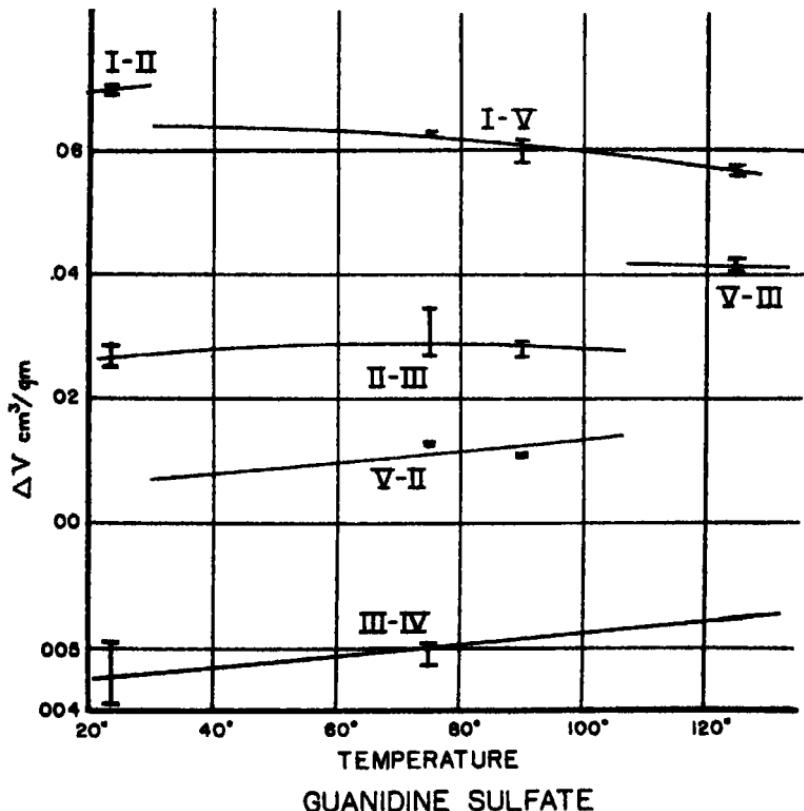


FIGURE 14 The volume changes of guanidine sulfate as a function of temperature

temperature and 125°, there is a complicated state of affairs at the lower pressures, but nothing else between about 10,000 and the maximum. The third set-up was with the 3/8 inch cylinder, in order to get more accurate values at low pressures, including the transition at 10,000. There are five modifications in all, the transition line at about 10,000 runs without interference with the others, but the other

transitions between 1,000 and 3,000 are so close together that it was a tax on the resolving power of the apparatus to separate them. Measurements were facilitated by the fact that the transitions all run cleanly at all temperatures in the range, with no appreciable region of indifference. There was, however, the usual decrease in the speed of the transitions at low temperatures. The measurement of the low pressure transitions was also facilitated by the fact that the changes of volume are of considerable magnitude.

TABLE VII  
TRANSITION PARAMETERS OF GUANIDINE SULFATE

Pressure kg/cm <sup>2</sup>	Temperature Centigrade	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
II-III					
3,170	20°	- 20	027	- 40	- 93
3,290	40	- 40	028,	- 22	- 52
3,310	60	+1 00	029	+10	+ 22
3,250	80		17	60	1 41
3,060	100		07	028	3 3
III-IV					
9,810	20°	- 050	0045	- 26	- 6
10,210	50	- 125	0048	- 12	- 3
10,300	75	+ 84	0050	+ 2	+ 05
10,170	100		119	0053	4
9,880	125		066	0055	8
Triple Points					
850	30°	I-II	117	071	4 3
		I-V	154	064	3 0
		V-II	037	007	1 3
2,950	107°	V-II	037	014	3 3
		II-III	- 042	028	- 5 9
		V-III	- 143	042	- 2 6

The phase diagram is shown in Figure 13, the changes of volume in Figure 14, and the thermodynamic parameters of the transitions in Table VII. The various values have been adjusted so as to satisfy the thermodynamic conditions of consistency at the triple points. It has been possible to do this without doing much violence to the independent experimental measurements, as the figures show, so that the values cannot be far wrong. However, in some cases it has been

necessary to make a pretty wide extrapolation of the experimental values for  $\Delta T$ , and there was therefore some latitude in adjusting the

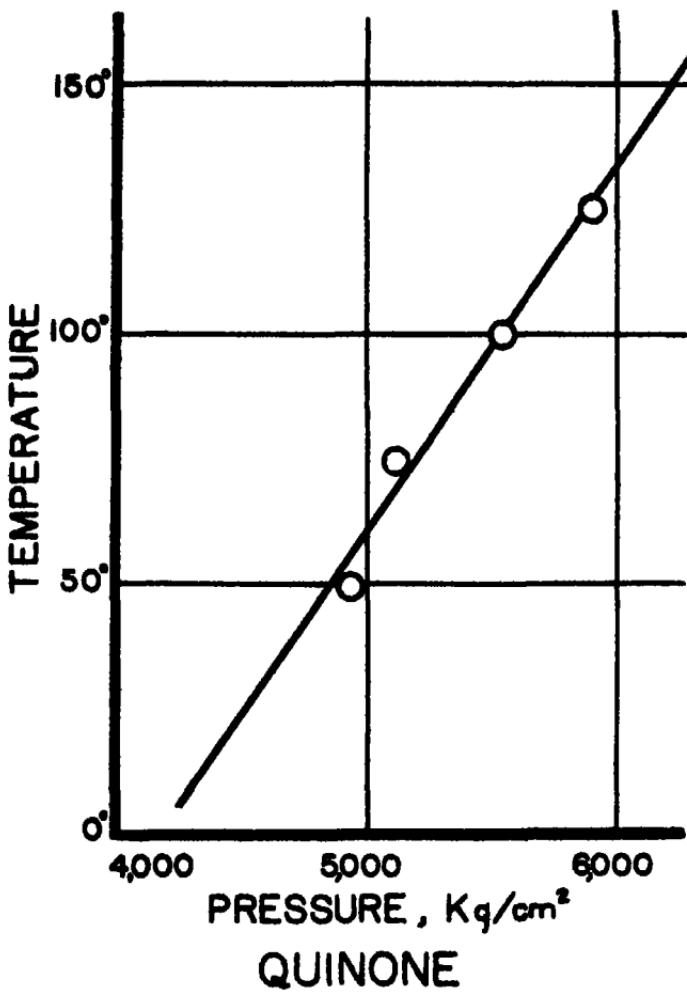


FIGURE 15 The transition pressures and temperatures of quinone

values to consistency I have not given in the table the parameters for the lines I-II, I-V, V-II, or V-III These lines are sufficiently characterized by the parameters at their triple points The lines II-III and III-IV appear to be curved, and detailed parameters are given for them in the table

*Quinone* Two set-ups were made one with the smaller and one with the larger diameter cylinder. With the first set-up runs were made at room temperature, 150°, and 100°. A fairly large transition was found at the lower pressures, but nothing else to the maximum. No attempt was made to measure the parameters of the transition with accuracy, but this was reserved for the set-up with larger diameter. With this, runs were made at room temperature, 50°, 75°, 100° and 125°. At the two lower temperatures the transition runs sluggishly, at room temperature the sluggishness was so great that no attempt was made to get accurate values for either transition pressure.

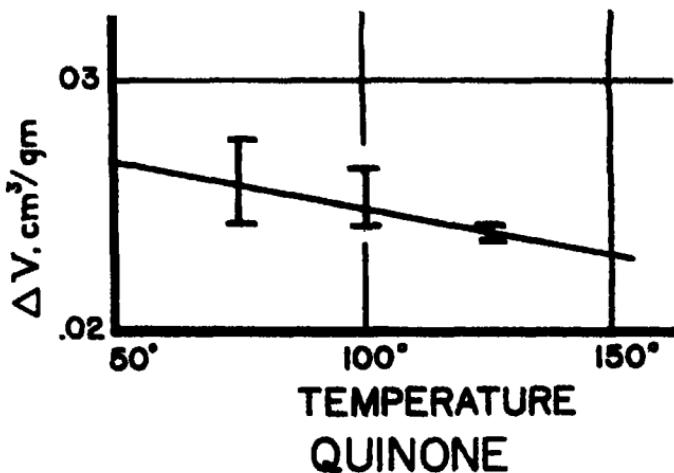


FIGURE 16 The volume changes of quinone as a function of temperature

or change of volume. At 50° good values for the transition pressure were obtained, but the sluggishness made difficult measurements of the volume change, which accordingly were not attempted. At the remaining temperatures, good values were obtained for both parameters, with both increasing and decreasing pressure. The band of indifference is without appreciable width at these temperatures.

The pressure-temperature diagram is given in figure 15, the change of volume in figure 16, and the transition parameters in Table VIII.

The shearing curve rises with marked upward concavity for most of its extent, to a shearing strength of 5,500 kg/cm² at 50,000. Quinone under pressure has the highest shearing strength of any organic studied. The concavity begins indefinitely around perhaps 8,000, and

this may be connected with the transition, but the indication of a transition in this region is much more ambiguous than usual with shearing, and probably its existence would not have been suspected without the volume measurements. At the upper end of the shearing curve, above 40,000, there is a gentle downward break, which suggests another transition not found with the volume apparatus.

*p-Dichloro-benzene* Four runs were made the seasoning run at room temperature, and three runs on the 2,000 kg-2 minute schedule at 50°, 100°, and 150°. Irregularities were found on all three runs which probably mean a transition with very small volume change, not more than 0.0006 cm³/gm. The transition is asymmetrical, and was more obvious with increasing than with decreasing pressure. It runs in the neighborhood of 23,000 at 50°, 30,000 at 100°, and 38,000 at 150°. It is not by any means improbable that there is another small transition near this one.

TABLE VIII  
TRANSITION PARAMETERS OF QUINONOL

Pressure kg/cm²	Temperature Centigrade	$\frac{dr}{dp}$	$\Delta V$ cm³/gm	Latent Heat gm cal/gm
4,860	50°	0.724	0.270	120 2.82
5,550	100	0.724	0.250	129 3.02
6,240	150	0.724	0.230	135 3.15

*Dichlorophenol* Three runs were made the seasoning run at room temperature, a run at 50°, and one at 125°. There appears to be a small transition at comparatively low pressures, running asymmetrically, being much more marked with increasing than with decreasing pressure. With increasing pressure a transition with volume change 0.0010 cm³/gm ran at 14,000 at 50°, and at 15,000 at 125° with the same change of volume. On decreasing pressure the curvature is too great to permit good values, but irregularities were found at both 50° and 125° at a pressure somewhat higher than would be expected from the results with increasing pressure. In addition, there is fairly good evidence of another transition at 46,000 at 50° with  $\Delta V$  equalling 0.0005, this is indicated by the readings with both increasing and decreasing pressure. At 125° there is also evidence of the same transition in approximately the same place, but the interpretation of the results is less satisfactory because of creep in the cylinder.

*Hydroquinone* In addition to the seasoning run at room temperature, runs were made at 150° and 175°. There is a small transition,

running fairly symmetrically, without perceptible region of indifference. This runs at 17,000 at 150° and 21,500 at 175°, with volume change of approximately 0.0010 cm<sup>3</sup>/gm. On the run at 150°, beginning at 28,000 or so, there was an irreversible decrease of volume extending over a pressure range of 6,000 kg/cm<sup>2</sup>. This might be either leak or decomposition. There was, however, no apparent change in the appearance of the material at the conclusion of the run, and since the transition found at 150° was also found at 175° (it is true at higher pressure) and since the direction of volume change is the opposite of a normal decomposition, the probability seems to be that it was leak.

The shearing curve of hydroquinone has a gentle change of direction at pressures too low to measure in the apparatus, which possibly may be the transition found above carried down to room temperature. The shearing curve rises smoothly with gentle upward concavity for its entire measured length, reaching a strength of 5,000 kg/cm<sup>2</sup> at a pressure of 50,000. This is unusually high for an organic compound.

*μ-Toluadine* Two runs were made—the seasoning run at room temperature, and one at 150°. Nothing was found at room temperature, but at 150° two transitions were picked up, with changes of volume too small to determine accurately. Both transitions were picked up with both increasing and decreasing pressure, so that there appears to be little doubt about their existence. The transition I-II runs between 34,600 and 36,100, and II-III between 38,000 and 42,200. The change of volume of the two transitions was approximately the same, between 0.0010 and 0.0015 cm<sup>3</sup>/gm.

*Naphthalene* Runs were made with two different fillings of the apparatus, the first gave three runs from room temperature to 150°, and the second five runs between the same temperature limits. There is a small, but perfectly unmistakable transition in the general neighborhood of 30,000, no other transition could be found up to nearly 50,000. Readings were made on a time schedule of 2,000 kg/cm<sup>2</sup> increase of pressure in two minutes. The change of volume was so small that it was hopeless to try to land on the transition, and the regular time schedule was maintained through the transition. The transition phenomena are unsymmetrical, the transition running much more sharply with decreasing pressure than with increasing. In fact, at 75° and lower the transition was not perceptible with increasing pressure, but showed up definitely enough with decreasing pressure. At higher temperatures the point where the transition began with increasing pressure could be located as a break in the direction of the isotherm, rather than as a discontinuity in volume. This asymmetry persisted to 150°.

The experimental values for the equilibrium points are shown in Figure 17. The point at 75° lies off the line, since this point is more difficult to determine because of sluggishness of the transition, it was ignored in drawing the most probable transition line. The values for change of volume were scattering, varying irregularly between 0.0013 and 0.0027 cm<sup>3</sup>/gm, 0.0020 is a fair enough average.

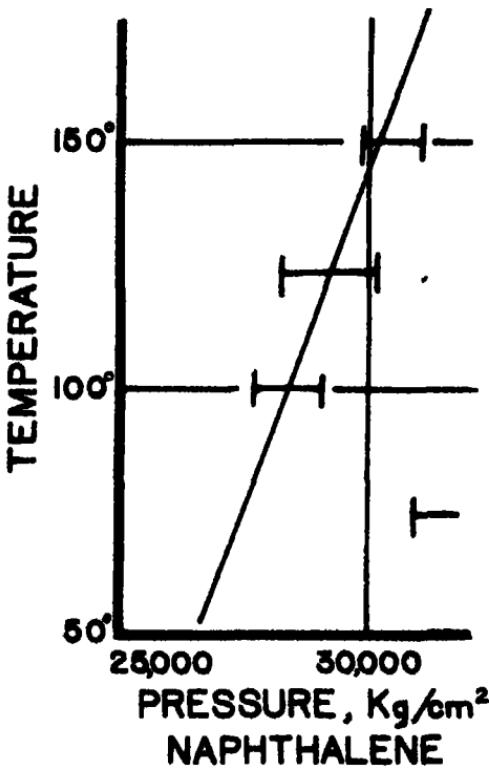


FIGURE 17 The transition pressures and temperatures of naphthalene

The accuracy of the points does not justify making a formal table for the parameters  $d\tau/dp$  of the line shown in Figure 17 is 0.0285. With the value for  $\Delta V$  just given this makes the latent heat of the transition vary from about 23 to 30 kg cm/gm.

The shearing curve has a gentle upward break between 25,000 and 30,000, which is probably the transition above. The general shape of the curve is gently concave upward, rising to a strength of 4,200 kg/cm<sup>2</sup> at 50,000.

*d-Camphor* This was the natural product I have already found camphor to have a very complicated phase diagram,<sup>6</sup> there being six modifications in the region between 0° and 200° and out to 12,000 kg/cm<sup>2</sup>. In the present work, certainly three, and probably more new modifications were found, making nine or more in all, so that camphor has the richest polymorphic phenomena of any substance yet investigated, the next richest being water, with seven forms under pressure, and an unstable form at atmospheric pressure.

More than two full weeks were spent in the measurements on camphor, with two different set-ups. With the first set-up, eight different runs were made at temperatures from room temperature up to 200° and up to the maximum pressure, 50,000. These runs gave a fairly clean cut transition in the general neighborhood of 30,000, with other transitions in the range from 10,000 to 20,000 which were capricious and most puzzling to interpret. There was no evidence of other transitions out to 50,000. A second set-up was accordingly made in a cylinder with piston 3/8 inch in diameter instead of 1/4, permitting the use of greater quantities of material, and thus greater sensitiveness. With this, most careful measurements were made in the range out to 20,000, making seventeen different runs altogether in the range from solid CO<sub>2</sub> temperature up to 140°. Two of these runs were made by the method of slowly varying temperature at constant volume, the others were the conventional isothermals. Most of the measurements with the second set-up were made with extreme care in steps of 400 kg/cm<sup>2</sup>, instead of the usual 2,000, so that the measurements were very time consuming. I think that the principal features of the pressure-temperature diagram are pretty well established by these measurements, although there are still some minor points, particularly in connection with the possible existence of unstable forms, which are not cleaned up. I was not willing to spend the much longer time that would have been necessary for this. Good values of  $\Delta V$  were not obtained, however. The changes of volume are in general small, much smaller than in the previous work at lower pressures, the transitions are sluggish, capriciously super- or sub-press., and the transition obtained depends on the history, new forms often not appearing, but instead the point obtained may be between two modifications out of their domain of stability, on an unstable prolongation of a transition line. For this reason all that could be done was to get very rough values for  $\Delta V$ , and no attempt at all was made to calculate the transition parameters. There is an additional complication, because when it is possible to combine transgressing the transi-

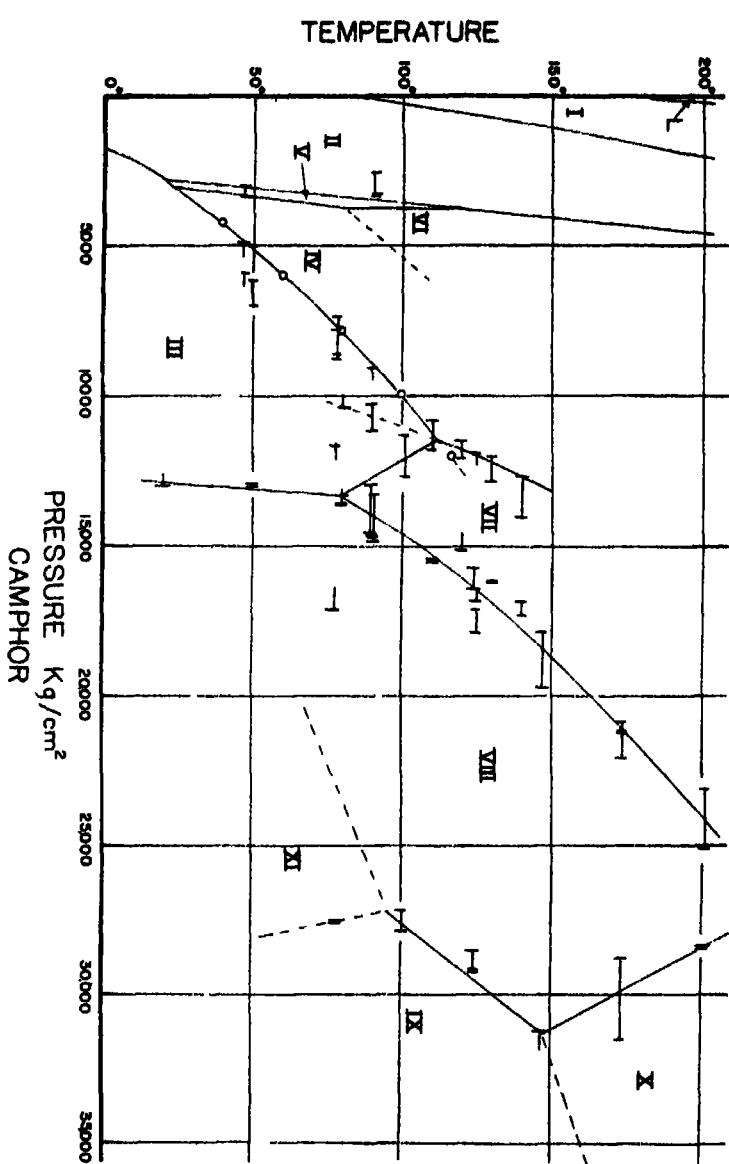


FIGURE 18 The transition pressures and temperatures of d-camphor. The modifications X and XI are not certainly established.

tion lines with a small interval of separation, there is the possibility of more than one transition running simultaneously in the apparatus. This doubtless occurred on several occasions.

The phase diagram ( $p-t$ ) is shown in Figure 18. There are certainly three new modifications, VII, VIII, and IX, and with very high probability another, X. The existence of X is made probable by the abrupt change in direction of the line VIII-IX above  $150^\circ$ , the fact that the transition is more sluggish at  $175^\circ$  than at  $125^\circ$ , alone very strong evidence for the appearance of a new phase, and the smaller values of  $\Delta V$  found at the two higher temperatures. The possible location of the hypothetical transition IX-X is shown dotted, if an experimental point could have been found on this line, of course the existence of the suspected modification would have been definitely established. It is also not at all improbable that the line VII-IX forks at the lower end, with a modification XI at lower temperatures; irregularities were found twice in the general region demanded by this.

Enough points were obtained on the line VII-VIII to make it highly probable that this line is not straight, but curved in the normal direction, as shown in the figure. VIII is distinctly more compressible than VII. The existence of the line IV-VII was not definitely established until measurements were made with the second set-up. At first I tried to force the transition points to lie on the known line III-IV. But the slope of the line was definitely wrong, and when points were obtained on the unstable prolongation of IV-VII into the region of III, the existence of the new phase VII and of the line IV-VII could no longer be doubted. After careful manipulation a couple of points were obtained on the line III-VII. III is not an easy phase to make appear, but IV or VII will usurp its place at the higher temperatures if either has been in the apparatus before. One has to approach the line from below and take pains not to get very far outside the region of existence of III if one wants to get it back again. The manipulations necessary to get this line involved holding the apparatus at pressures near 12,000 and at temperatures near  $100^\circ$  for a couple of days. Two points were obtained on III-VIII without great difficulty after the apparatus had been held at room temperature over night at low pressures to give III a chance to appear. At solid  $\text{CO}_2$  temperature, pressure was increased from atmospheric to 12,000 without the transition to III running, but on warming, the internal viscosity became low enough to permit the transition to run with decrease of volume. A few points were also obtained on III-IV and on II-IV by way of orientation. The sensitiveness was not great enough to permit establishing the existence of V.

The following values of  $\Delta V$  are very rough. In general, the order of magnitude of  $\Delta V$  found with these two set-ups was only one half that found in the previous work to 12,000. On the line VIII-IX,  $\Delta V$  is probably between 0.0025 and 0.0030 cm<sup>3</sup>/gm. On the hypothetical VIII-X,  $\Delta V$  drops to between 0.0015 and 0.0020. On IV-VII,  $\Delta V$  is a very strong temperature function, decreasing from something of the order of 0.03 at 80° to perhaps 0.005 at 130°. At the triple point III-IV-VII, previous measurements gave for  $\Delta V$  III-IV about 0.020.  $\Delta V$  IV-VII must be larger than 0.020 at the triple point. No values of  $\Delta V$  worth recording were obtained for III-VII. On the line VII-VIII,  $\Delta V$  also appears to be a strong temperature function, varying with temperature in the inverse sense from that of IV-VII. From 80° to 200°,  $\Delta V$  on VII-VIII increases perhaps from 0.005 to 0.015. Nothing worth recording was obtained for III-VIII.

One must be prepared for a more complicated state of affairs in camphor than in the simple phase diagrams of inorganic compounds. The great variation of  $\Delta V$  along the transition lines is an example. As far as these measurements go, there is no definite evidence that the line IV-VII does not end in a critical point, an unprecedented state of affairs for a solid-solid transition. The sluggishness of the transitions is so great that there is no experimental evidence that the transitions may not be spread over a range, instead of taking place at a single well defined point. The possibility of various complexities suggested by recent discussions of transitions of the second, third, and higher orders must be kept in mind. Another possibility of complication presents itself in the fact that natural camphor is dextro-rotary, conversion to a left handed or a racemic form is to be kept in view. However, a measurement of the optical rotation, which I owe to the kindness of Professor Kohler, showed no difference within about 1 per cent limit of error between the rotation of the original specimen and the specimen used in the first set-up, which had been exposed to 50,000 and 200°.

The general course of the shearing curve of camphor is gently concave upward, but with three dips in the neighborhood of 7,000, 22,000 and 35,000 kg/cm<sup>2</sup>. These dips doubtless correspond to the transitions above, but the correspondence is not close. The shearing strength at 50,000 is 4,200 kg/cm<sup>2</sup>.

*Menthol.* In addition to the seasoning run at room temperature, runs were made at 75°, 100°, and 150°. There are probably at least three transitions, but the volume changes are not large, and they are sluggish at all temperatures, so that it would have been a matter of

very great difficulty to get data sharp enough to determine the transition parameters with any precision, and I let the matter go after

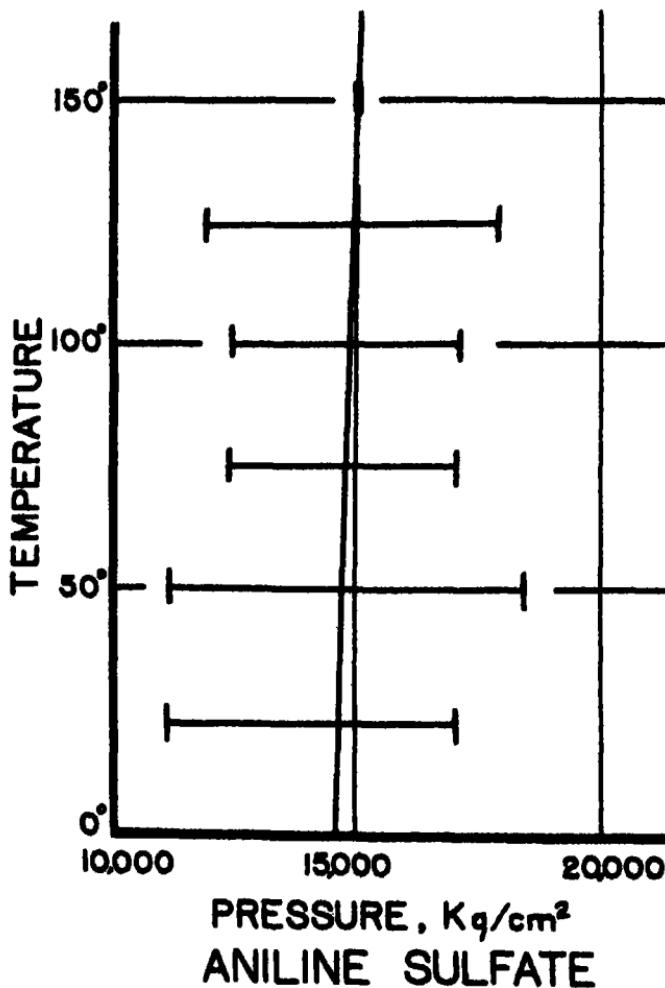


FIGURE 19 The transition pressures and temperatures of aniline sulfate

more or less superficial examination. The transitions occur in the general neighborhood of 15,000, 30,000, and 42,000 kg/cm<sup>2</sup>, and the transition lines run approximately vertically, with small latent heat. The two lower transitions are spread over a range of 7,000 to 10,000

$\text{kg}/\text{cm}^2$ , and the upper transition over perhaps one half as much. The changes of volume are of the general order of  $0.005 \text{ cm}^3/\text{gm}$ .

At atmospheric pressure it is known that menthol supercools very readily, and the crystallization phenomena are very sluggish. At one time I spent much effort in trying to produce large single crystals by crystallization from the sub-cooled melt, but with no luck whatever. The sluggish behavior under pressure is thus what might be expected.

*Aniline Sulfate.* Six runs were made with a single set-up, from room temperature to  $150^\circ$ . There is a single transition, running nearly vertically at approximately 15,000. The transition is highly unsym-

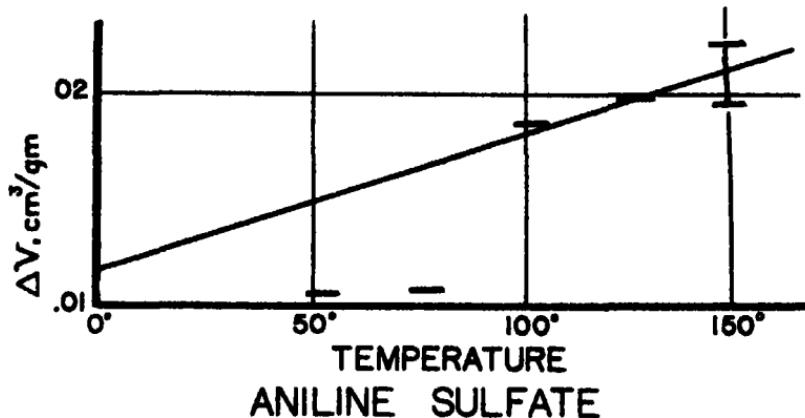


FIGURE 20 The volume changes of aniline sulfate as a function of temperature.

metrical, running much more sluggishly with increasing than with decreasing pressure. At the lower temperatures it was not possible to make settings on equilibrium, but measurements were made on a regular time schedule straight through the transition, and the beginning of the transition was detected by a slight break in direction of the isotherm. It was curious that the break in direction was not accompanied by a corresponding increase in creep. Because of the sluggishness, good values of  $\Delta V$  could not be obtained at the lower temperatures. At higher temperatures the transition became sharper, permitting better values of  $\Delta V$  with decreasing pressure. However, only at the highest temperature,  $150^\circ$ , was it possible to get values of  $\Delta V$  with both increasing and decreasing pressure, and to set on equilibrium in the conventional way. Below  $150^\circ$  the band of in-

difference had a nearly constant width, and then at 150° the band narrowed to zero in an unusual way.

The pressure-temperature diagram is given in Figure 19, the changes of volume in Figure 20, and the transition parameters in Table IX.

TABLE IX  
TRANSITION PARAMETERS OF ANILINE SULFATE

Pressure kg/cm <sup>2</sup>	Temperature Centigrade	$\frac{d\tau}{dp}$	$\Delta V$ cm <sup>3</sup> /gm	Latent Heat kg cm/gm	gm cal/gm
14,500	0°	3	012	11	3
14,750	75	3	016	19	5
15,000	150	3	021	30	7

There is obviously much uncertainty in  $\Delta V$  and latent heat at low temperatures.

The shearing curve has a very definite upward break at 19,000, doubtless due to the transition above. Below and above the break the shearing curve is concave to the pressure axis. There is a second small upward break at 40,000. One suspects another modification at high pressures, suppressed in the volume apparatus by the same sluggishness that is so characteristic of the transition at 15,000. The shearing strength at 50,000 is 2,700 kg/cm<sup>2</sup>. The general appearance of the shearing curve is linear, the curvature of the three different segments being only slight.

#### SUBSTANCES GIVING NEGATIVE RESULTS

The list of negative substances is surprisingly short in comparison with the number of negatives found among the inorganics.

*Chloral Hydrate* Exploration to about 50,000 at room temperature and 45,000 at 150° in steps of 2,000 kg/cm<sup>2</sup> on the one minute schedule.

*Trichloroacetamide* Exploration to 50,000 at room temperature and 47,000 at 125° in steps of 2,000 kg/cm<sup>2</sup> on the one minute schedule.

*Guanidine Nitrate?* Exploration at room temperature as in the last two examples. On trying for the exploration at 150°, the cylinder ruptured near the top and initial pressure, so that the evidence for or against a transition at this temperature is very meagre. The apparatus was not set up again.

*Nitrourea* Three different set-ups were made with this. The first gave nothing at room temperature. Pressure was raised to 30,000 before raising temperature to 150°. From here pressure was raised to 45,000, and then released. A moderate sized transition appeared

to run at 30,000 on releasing pressure. At very low pressures there was some large volume increase. On again increasing pressure there was a large and abnormal decrease of volume in the low pressure range, then normal behavior up to 35,000, where the cylinder broke. The first repetition yielded nothing again at room temperature nor at 75° to 45,000, but on heating under 10,000 to 118° the contents exploded. A second repetition also yielded nothing on the seasoning run at room temperature. Pressure was now increased to 20,000 before raising temperature to 125°. Nothing new was found to 47,000. On releasing pressure volume creep (increase) started at 20,000. The direction of pressure change was at once reversed to an increase, and small steps made back to 40,000, but no reverse transition found, and there was a permanent increase of volume over the first excursion. The probability is then that there is no reversible transition, but the decomposition phenomena are complex. If the substance is heated at low pressures it explodes, but if heated at higher pressures there is non-explosive decomposition with increase of volume. There is an intermediate range of pressure in which the relation between the two types of decomposition is not simple.

*Phenol* This is listed among the negative substances, although it is already known to have a transition in the general neighborhood of 2,000, because no further transitions were found with the present apparatus. Exploration was made to 50,000 at room temperature and to 45,000 at 150°, in steps of 2,000 on the one minute schedule.

Exploration with the shearing apparatus gave a pronounced knee at about 10,000, then nearly linear rise, but with slight upward concavity, to 3,300 at 50,000.

*Anthracene* Exploration was made at room temperature and 150°. At room temperature the region between 20,000 and 34,000 was explored with particular care, taking readings every 400 kg, five times as many as usual. Nothing was found at either temperature.

The shearing curve takes a pronounced upward bend between 22,000 and 30,000, leading to the expectation of a transition. Below 25,000 the shearing curve is concave downward, above 25,000 concave upward, rising steeply to a shearing strength of 4,000 kg/cm<sup>2</sup> at 45,000. Between 45,000 and 50,000 the shearing curve turns and runs horizontally. This doubtless corresponds to the permanent change found at the termination of the shearing experiments, the anthracene being altered to a substance of deep purplish black color. This is the most strikingly obvious example found of an irreversible change of an organic substance by shearing. There was no obvious permanent

alteration in the material which had been exposed to hydrostatic pressure without shear

#### SUMMARY OF SHEARING MEASUREMENTS ON SUBSTANCES NOT INVESTIGATED IN VOLUME APPARATUS

The arrangement in the following is alphabetical

*Acetanilide* Shearing curve nearly linear over entire length, rising to 2,800 kg/cm<sup>2</sup> at 50,000

*Azizarin* Measurements were made only to 35,000, where the piston of the shearing apparatus broke. The shearing curve is gently concave toward the pressure axis up to 14,000 where there is an inflection, with gentle upward curvature beyond. The shearing strength at 35,000 is 1,800 kg/cm<sup>2</sup>. A transition in the neighborhood of the point of inflection suggests itself.

*Imidol* Shearing curve smooth, and with pronounced concavity toward the pressure axis over the entire length, rather unusual in an organic. The shearing strength at 25,000 is 2,600 kg/cm<sup>2</sup>, and 3,900 at 50,000.

*Aniline Hydrochloride* Beyond the "knee" at very low pressures the shearing curve is practically linear over its entire length, rising to 3,100 kg/cm<sup>2</sup> at 50,000.

*Anthraquinone* The shearing curve is nearly linear up to 25,000, beyond this it rises with rapidly increasing upward curvature, reaching 3,300 kg/cm<sup>2</sup> at 50,000.

*Dinitrotoluene* The shearing curve rises with gentle upward curvature to about 25,000, beyond which it rises linearly, reaching 2,900 kg/cm<sup>2</sup> at 50,000. Repetition gave essentially the same results.

*Guanidine* The shearing curve is nearly linear beyond the knee at low pressures, and rises to 2,500 at 50,000. It is thus one of the weaker organic substances.

*Picric Acid* The shearing curve rises with marked concavity toward the pressure axis, with increasing approach to linearity at the higher pressures, to 2,500 at 50,000.

*Tartaric Acid* The shearing curve rises with gentle concavity toward the pressure axis to 5,000 kg/cm<sup>2</sup> at 50,000, the highest shearing strength found for any organic substance except quinone.

#### SUMMARY

Transition data are presented for twenty-five organic substances in the pressure range up to nearly 50,000 kg/cm<sup>2</sup> and at temperatures between room temperature and 150° or 200°. It is obvious that our

theories of the structure of solids are not yet sufficiently advanced to justify an attempt to predict theoretically the values of the various transition parameters, so that for the present the material of this paper will have to be used qualitatively to suggest the general nature of the phenomena. As already suggested, polymorphism in the temperature range of this work is of much more frequent occurrence among organic than inorganic substances, but on the other hand the transition phenomena are less clean cut and definite, and are accordingly more difficult to measure. It is highly probable that a number of small transitions have been missed in the work above. The transitions of organic substances are in many cases highly unsymmetrical with respect to pressure above and below the equilibrium point. The statistical number of new transitions does not seem to be distributed as uniformly over the entire pressure range as it is with inorganics, there being too few at the higher pressures, and furthermore transitions with the larger volume changes seem to be disproportionately few at the high pressures. This is consistent with the very great increase in viscosity of organic substances to be expected at high pressure, as suggested both by measurements on the viscosity of organic liquids and on the shearing of organic solids. The effect is doubtless an interlocking effect, which will be more important with the more complicated molecules.

In addition to the transition measurements in the above, a study has been made of the shearing of a few organic substances as a function of pressure, and rough numerical data are given. The shearing curves of organics are much more frequently concave upward than those of inorganics, the explanation is doubtless the interlocking effect just mentioned.

I am indebted to my assistant Mr L H Abbot for most of the readings, and for financial assistance to the Rumford Fund of the American Academy of Arts and Sciences, and to the Milton Fund of Harvard University. Comparatively prompt publication has been made possible by the Francis Barrett Daniels Fund of Harvard University.

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## REFERENCES

- <sup>1</sup> P W Bridgman, Proc Amer Acad **71**, 387-480, 1937, Phys Rev **48**, 825-847, 1937
- <sup>2</sup> P W Bridgman, Proc Amer Acad **51**, 90, 1915
- <sup>3</sup> P W Bridgman, Proc Amer Acad **52**, 106, 1916
- <sup>4</sup> Reference 3, page 97
- <sup>5</sup> F Körber, ZS Phys Chem **82**, 45-55, 1913
- <sup>6</sup> Reference 3, page 110

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**MELANOPHORE RESPONSES IN THE YOUNG OF  
MUSTELUS CANIS**

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**WITH TWO PLATES**



# MELANOPHORE RESPONSES IN THE YOUNG OF MUSTELUS CANIS

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## I INTRODUCTION

THE study of the color changes in elasmobranch fishes has been much handicapped by the relatively large size of these animals and the consequent difficulty in keeping them in laboratory tanks and other containers during protracted study. In this respect the young or so-called pups of the viviparous smooth dogfish, *Mustelus canis*, are much more favorable for investigation than are the adults. These young, born during the brief summer period for this species at Woods Hole, have a convenient length of some 25 to 30 centimeters and even at birth are endowed with a fully active melanophore system responsive in its color changes to a degree even beyond that of the adult (Parker, 1936b). They are, moreover, unusually hardy and recover from operation with success. Hence they are a most satisfactory elasmobranch for study. In the following paper a number of the aspects of color change in these young fishes will be discussed, aspects that can be approached much better in them than in the adults.

The work herein recorded was carried out at the Oceanographic Institution in Woods Hole on material supplied for the most part by the Marine Biological Laboratory of that place. The investigations were greatly facilitated by the use of two large open-sea fish-cars 15 by 15 by 4 feet, so built that they could withstand reasonably rough water. They were supported by floats and attached to the inside of the pier of the Oceanographic Institution, where an excellent circulation of sea-water was to be had. The cost for the construction of these cars was defrayed by a grant from the Permanent Science Fund of the American Academy of Arts and Sciences. To the officers of this Fund and to those of the two Laboratories named I am under great obligation for hearty cooperation and assistance.

## II METHODS

No special methods were employed in this study. The pups, before they were operated upon, were stupefied by immersion for ten or more minutes in a mixture of sea-water and ice, a method which may be variously modified and which has many advantages for cold-

blooded vertebrates (Parker, 1938) In most experiments the pups were tested in one of two large sea-water tanks in the basement of the Oceanographic Institution These tanks measured 4 by 4 by 2 feet and were painted inside, one white and the other black They were illuminated continuously by overhead, 100-watt, electric lights The black tank could be covered by a movable black roof by which it could be rendered fully light-proof Both tanks were provided with an ample and continuous supply of fresh sea-water

### III BLINDING

The adult smooth dogfish, when blinded, follows the general rule for the majority of chromatic vertebrates (Parker, Brown, and Odiorne, 1935) and because of the expansion of its melanophores, assumes a dark tint (Parker and Porter, 1934) In this respect it differs somewhat from other elasmobranchs In eyeless *Raja brachyura*, according to Hogben (1936), the melanophores are neither fully expanded nor fully contracted, and in the related batoid *Urolophus* no color change could be discerned by Griffiths (1936) during the four hours that followed enucleation In *Torpedo marmorata* Veil and May (1937) observed that the usual brownish tint of this species was maintained unchanged as well without the eyes as with them Possibly some of these negative results may disappear when means have been devised for the better handling of these fishes But whatever such final results may be on other elasmobranchs the adults of *Mustelus canis* on the loss of their eyes darken so quickly and so regularly that this change must be attributed to the blinding of these fishes

The normal pups of *Mustelus*, like the adults, take on tints fully pale or fully dark according to their illuminated environments These changes occur somewhat more rapidly in the pups than they do in the adults They ordinarily take place in a relatively few hours, the change to the dark condition being accomplished in less time than that to the pale one

In the initial experiments six pups, which were known to be fully capable of color change, were blinded by having their optic nerves cut This operation was easily accomplished by buccal incisions The pup after stupefaction by cold was held ventral side up and with the mouth widely open The points of a pair of small scissors slightly separated were pressed through the membrane and cartilage on the roof of the mouth and into the rear of the orbit so as to include between the blades the optic nerve as it leaves the eye-ball By a single cut of the scissors this nerve could be easily severed and after

a similar operation on the opposite side of the head the pup was assumed to be completely blinded. Such operations were almost bloodless. The operated pups on recovery swam normally except that they collided continually with the walls of the tank or with other obstacles showing that they were in reality without vision.

Of the six pups thus treated three were put in the large, white-walled illuminated tank and three in the black-walled one. After half a day the two sets of fishes were compared. In both sets the individual pups were obviously dark as attested not only by ordinary inspection, but also by the state of their melanophores as seen under the microscope (Fig. 4). The two sets were, however, indistinguishable and both were much darker than normal pale pups in the white-walled tank (Fig. 2), but not as dark as normal dark ones in the black-walled tank (Fig. 1). I never saw blinded pups reach so deep a tint as was occasionally observed in blinded adults (Parker and Porter, 1934). The blinded pups were nevertheless always to be classed as dark individuals and the fact that the two sets, one in white and the other in black surroundings, were indistinguishably dark shows, as might have been expected, that the eyes are essential for responses to environmental illumination.

The six blinded pups were now redistributed in that three were put in the white-walled illuminated tank, and three in the tank from which all light was excluded. After seven hours it was obvious on quick inspection that the three pups in darkness were all somewhat paler than any of those in the illuminated tank, a condition that was still somewhat more striking after twelve hours when both to the unaided eye and under the microscope (Fig. 3) the blanching of the blinded pups in darkness was obvious. A cut was now made in the pectoral fin of one of each of the two sets of pups and in half an hour a band of maximum paleness had appeared on each fin. Thus a cut in the fin of a blinded pup may produce a local maximum blanching like that which occurs over the whole of a normal pup with functional eyes and in illuminated white surroundings. In this respect the cut may be said to be a substitute for the eye.

As a final step in this series of tests the three blinded pups that had been kept in darkness were now transferred to the white-walled illuminated tank and those that had been in the illuminated tank were placed in darkness. After five hours the three pups in darkness were all found to be paler than those in the light, the two sets having thus reversed their tint with the change in illumination. From this observation it is evident that blinded *Mustelus* pups have not entirely

lost their power to change in tint, for they are consistently darker in bright light than in darkness.

The effect of the pituitary gland on these color changes was next taken up. The buccal operation by which Lundstrom and Bard (1932) removed the pituitary complex from the adult *Mustelus* through an aperture cut in the cartilage of the roof of the mouth is very easily applied to the pup. By this procedure the pituitary glands were excised from four pups and these young fishes were then put two in a dark-walled illuminated tank and two in a white-walled one similarly lighted. Both sets of pups gradually blanched and after twenty hours both reached what appeared to be maximum paleness. When their pectoral fins were inspected under the microscope, the melanophores of these parts were found to be fully punctate (Figs. 5 and 6), and it was obvious that their pigment could undergo no further concentration. I therefore assumed that their melanophore pigment had reached a state of complete concentration and that this state was dependent upon the absence of the pituitary gland and independent of the nature of the illuminated environment. Two of these hypophysectomized pups were then put in complete darkness and two in the white-walled illuminated tank. After seven hours these two sets of pups were still maximally pale and indistinguishable. The optic nerves of all four fishes were then cut by the operation already described and the pups were set aside in the black-walled tank for inspection. At this stage one of the pups escaped from the tank during the night and died on the floor of the tank room. The remaining three, however, were kept in the tank and under inspection for over a day and during this time they all persisted in remaining fully pale. At the end of this time the test was judged concluded though the experimental fishes lived three to four days longer. During this final period cuts were made in some of their uncut pectoral fins with the results that no pale bands whatsoever appeared. The skin in these fishes was apparently fully pale before the cuts were made and was not open to further blanching. This question was tested further by removing the pituitary glands from two new pups and, after about a day when the pups had become very pale, by cutting their pectoral fins. The regions where bands might have appeared were, however, not paler than the rest of the fish showing that the loss of the pituitary gland was in itself sufficient to induce maximum blanching.

It is well established that a smooth dogfish blanched by hypophysectomy can be darkened temporarily by the injection of an extract from the intermediate lobe of the pituitary gland (Lundstrom and

Bard, 1932, Parker and Porter, 1934) The activating substance contained in this extract and commonly designated as intermedin is believed to be the normal means of darkening the fish. The control of this substance must be dependent upon the fish's eye. When the retinal field of the fish is stimulated by light from an environment of dark coloration, the activating substance is liberated from the gland and when the field is stimulated by light from whitish areas, the discharge of this special material is inhibited. These responses can be shown to occur in the pups as they do in the adults. It has been further pointed out in this paper that pups in which the pituitary glands are still intact, but which have been blinded by the severance of their optic nerves, are quite dark in bright light and not so dark in darkness. So far as is known, these changes depend upon the activity of the pituitary gland, for they disappear with its loss. Since they occur in blinded pups, they imply the action of some other receptor than the eye. That they do not depend upon some hormone given out by the eyeball itself, such as has been found by Kropf (1929) in certain melanophore reactions in tadpoles, is seen in the fact that they occur as well in enucleated pups as in those blinded by the simple severance of the optic nerves. But where the activating receptors are to be found I have been unable to discover. Somewhere in the body of *Mustelus* there must be receptors which, when stimulated by light, induce a discharge of intermedin and when enveloped in darkness inhibit that discharge, or in some other way induce these mild responses. In this respect *Mustelus* appears to be in the same category as certain other vertebrates such as the minnow *Phoxinus* (von Frisch, 1912, Scharrer, 1928), the catfish *Amerurus* (Abramowitz, 1936), possibly the lamprey (Young, 1935) and even the frog (Rodewald, 1935).

#### IV BLANCHING

The blanching of elasmobranchs, as Waring (1936) remarks, is far from being fully understood. Adrenalin, one of the most universally effective agents in the concentration of melanophore pigment, was found by Young (1933) to be without influence on the tints of *Scyllium* and of *Torpedo*. Wykes (1936) obtained from this agent only a slight blanching in *Raja* and *Rhina*. *Mustelus* on the other hand blanches readily to adrenalin (Lundstrom and Bard, 1932, Parker and Porter, 1934, Parker, 1935b, 1936a, 1936b), though from the very heavy dosage necessary for this effect it is doubted by some workers (Lundstrom and Bard, 1932) whether this response may not be due to vasoconstrictor changes rather than to a direct influence on the melan-

phores. The fact that the defibrinated blood from a pale *Mustelus* is without effect when injected under the skin of a dark one (Parker and Porter, 1934) makes it probable not only that adrenalin is not normally concerned in the blanching of this dogfish, but also that any blood-borne agent such as the W-substance hypothesized by Hogben (1936) for the blanching of certain other elasmobranchs, does not occur in *Mustelus*. Thus far the only known normal method of blanching for *Mustelus* is that dependent upon concentrating nerves (Parker and Porter, 1934), a method which appears to be peculiar to this dogfish, for, up to the present, it has not been found to any extent in other elasmobranchs.

The nervous blanching of *Mustelus* has been shown to be due to an oil-soluble hormone, a lipohumor, produced by the concentrating melanophore nerves of this fish (Parker, 1935b, 1936c). Is it not possible that this animal possesses other means of becoming pale than that just mentioned? *Mustelus* like most other fishes dies pale, a condition which is generally attributed to the lack of available oxygen for the melanophores when the circulation of blood ceases. This, however, is not likely to be a natural means of blanching, though it is conceivable that by vasomotor disturbances it might play a part in inducing such a change. Much more probable as a means of blanching would be the removal from the fish's blood of the pituitary secretion by which the dispersed state of the melanophore pigment was induced.

For experimental tests of this question *Mustelus* pups are especially well adapted. If a strong cord is tied firmly and tightly around the head of a dark pup at the level of the posterior margins of the eyes and another at the level of the vent, the pup will be divided into three regions: an anterior one which in consequence of the ligating cord is without circulation, a posterior one also without circulation, and a middle region containing the heart and connecting vessels, and in which in consequence of the presence of these organs a circulation of blood still goes on. A dark pup so divided will remain dark for a full hour. If in a freshly ligated pup the pericardium, which is of course in the middle region, is opened and an irrigation canula is tied into the ventral aorta, the middle region can be washed free of blood in some five minutes by a current of Ringer's solution. During the washing this region blanches very completely and remains so indefinitely (Fig. 7). This test was made on four pups and always with the same result. Under the microscope the melanophores of the middle region could be seen to be reduced almost to the punctate state (Fig. 9), while those of the anterior and the posterior regions remained

with dispersed pigment (Fig. 8). Plainly the washing out of the blood with its contained intermedin from the middle region is the occasion of its blanching.

That this blanching is not due to the death of the tissues concerned is seen in the fact that when a middle region blanched in the way described is further irrigated with a mixture of one volume of Ringer's solution and two volumes of commercial pituitrin, this middle region again darkens in about a quarter of an hour through the dispersion of its melanophore pigment. Hence I conclude that *Mustelus* may blanch in consequence of the loss of the pituitary dispersing neurohumor. Since it also blanches through nerve action and in death, this fish may be said to possess three ways of accomplishing this end. The illumination of the retina with light from a pale tinted environment probably not only excites the concentrating nerve fibers to produce their appropriate neurohumor, but it may also inhibit the discharge of the dispersing neurohumor from the pituitary gland.

The melanophores of a denervated area on a blinded, hypophysectomized *Mustelus* in darkness would seem to be as near freedom from stimulation as could easily be imagined. In fact, in discussing this condition in *Amerurus* Abramowitz (1936) with a certain degree of caution has called attention to exactly this state as one devoid of stimulation. Such an interpretation would seem quite reasonable except for the fact that in *Mustelus* the state just described leads to a condition of complete concentration of melanophore pigment (palleness), whereas in *Amerurus* it induces precisely the opposite state (dark coloration). If, as Abramowitz suggests, it is the property of an unstimulated melanophore in *Amerurus* to disperse its pigment nearly to fullness, it must be admitted that it is the property of a *Mustelus* melanophore under like conditions to concentrate its pigment. The understanding of such a situation is by no means easy. It is conceivable that all cells called melanophores are not really alike, an opinion for which much might be said. It is also possible that we have not yet exhausted all the sources of stimulation and that *Mustelus* and *Amerurus* in the conditions described illustrate the action of certain opposing activators as yet undiscovered. These conditions come very close to the problem formerly discussed for chromatophores concerning states of rest and of activity. What are to be described as these states in chromatophores I have elsewhere analyzed (Parker, 1935c) and I still see no reason to change my opinion that it is best to describe the active chromatophore as one in which the pigment is moving and the resting one as one in which the

pigment is quiescent. Certainly melanophores whose nerves have been recently cut and whose pigment is in consequence dispersed are not in a state of paralytic rest as was at one time believed (Parker, 1936c, 1936d). Hence I hold to my former view as to rest and activity. Though it is perhaps premature to make a decision, I am inclined to look upon the conditions of the melanophores in *Mustelus* and in *Amerurus* just described as due to novel and thus far undiscovered means of stimulation rather than to innate and fundamental differences of type in their organization.

#### V THE NERVOUS CONTROL OF *Mustelus* MELANOPHORES

*Mustelus* is peculiar among elasmobranchs in that its pale phase is under the control of nerves. This was first demonstrated by Parker and Porter (1934) in a series of experiments in nerve cutting. Whenever a cutaneous nerve in this dogfish is cut a blanched area corresponding to the peripheral distribution of the nerve in question appears. In place of the excitation supplied by a cut, faradic stimulation will also induce peripheral blanching (Parker, 1935a). In these tests, however, nerves were not freed and directly stimulated, but the electric current was applied to the tissue through which the nerves passed. In pups it is possible to expose just dorsal to the pectoral fin the nerves of the brachial plexus and a single one of these can be lifted and placed under the electrodes of an induction apparatus. In a dark pup so prepared no color change occurs until the current is made when, after some fifteen minutes of stimulation, a faint irregular pale area will develop in that part of the fin to which this particular portion of the brachial plexus is distributed. This area is by no means so well defined nor so fully pale as that produced by cutting nerves nearer the periphery of the fin, but its presence is unquestionable and its position appropriate. Its partial vagueness is due undoubtedly to the irregular spread of the nerve fibers in the particular branch stimulated as compared with the more regular and limited distribution of the smaller branches which are severed by a peripheral cut in the fin. Electric stimulation applied to a nerve in the brachial plexus of a fully pale dogfish pup is followed by no observable color change in the fin. Thus faradic stimulation applied to an isolated nerve in a dark pup results in the same general effect, blanching, as the cutting of nerves in the fin does. This conclusion is at first sight not in agreement with that of other workers who have attempted the electric stimulation of melanophores and their nerves in elasmobranchs. Schaefer (1921) was not able on the application of faradic

stimulation to the skin of *Raja clavata* to elicit responses from its melanophores. Nor was Wykes (1936) successful in obtaining a response on applying a similar stimulus to the spinal nerves, haemal arches, and skin of *Raja*, of *Rhina*, and of *Scyllium*. But in none of these fishes is there any reason to suppose that the melanophores are subject to nervous activation. In fact there is very good ground for assuming that they are not so controlled and if this is true, it is very improbable that electric stimulation of nerves distributed to a given area would have any effect whatever on the melanophores of such an area.

In contributions recently published on the antidromic responses in *Fundulus* (Parker, 1936e, 1937a) I have shown that the melanophore nerve fibers when stimulated by a cut not only excite the melanophores distal to the cut, but also activate those proximal to it. This antidromic action was to be expected though evidence of it is not always easily discoverable. In the various experiments on *Mustelus* pups I attempted repeatedly to test these fishes for antidromic responses, but my efforts were invariably unsuccessful. Though for tests of this kind *Mustelus* would appear to be more favorable than *Fundulus*, I have been unable to carry such tests to a successful issue. Nevertheless I am convinced that in *Mustelus* antidromic action ought to be demonstrable.

In 1935 and in 1937 I showed that an ether extract of the fins and skin of pale smooth dogfishes yielded a material that when injected under the skin of a dark fish excited in it a pale spot due to the concentration of pigment in the local melanophores. The effective material in this extract was found to be soluble in olive oil and in ether, though not in water, it would withstand heat to 110° C., boiling with weak alkali and with weak acid. It was therefore shown to be a relatively stable substance. In the summer of 1936 I collected a considerable quantity of pale *Mustelus* fins and skins and kept them in glass over the period of a year. At the beginning of this season (1937) I extracted a reasonable amount of these skins and fins and under appropriate conditions I injected some of this extract under the skins of several dark *Mustelus* pups. They all showed characteristic secondary blanching (Fig. 10) and thus demonstrated the efficiency of the extracted substance even after a year's standing. These observations confirm the opinion already expressed that this *Mustelus* lipohumor is a fairly stable substance.

Having prepared this crude extract in some quantity, I proceeded to test it on other vertebrates, namely on the catfish, *Ameurus*

*nebulosus*, and on the common frog, *Rana pipiens*. In both instances three dark individuals and three pale individuals received in each case 0.05 cc. of the crude oily extract mixed with an equal volume of Ringer's solution and shaken into a coarse emulsion. In *Amerurus* this mixture in proper amount was injected under the skin of the flank of the fishes on their right sides, and in a corresponding position on their left sides an equal amount of Ringer's solution was introduced as a control. Similar injections were made under the skin of the calves of the six frogs, the emulsion into the right calves, and the Ringer's solution into the left ones.

The three pale catfishes were kept in a white illuminated vessel and remained unchanged for about an hour after the injection had been made, when a well marked dark spot appeared in the skin of each fish directly over the region of injection. These spots persisted for about three and a half hours, when one of the catfishes was preserved in formol-alcohol as a demonstration (Fig. 11). No marks of any kind appeared over the regions into which only Ringer's solution had been injected. The two catfishes still living were then injected each with 0.2 cc. of adrenalin 1:1000. In a little less than an hour both fishes were very pale and the dark spots originally on them had fully disappeared. Four hours after the injection of the adrenalin and presumably after it had disappeared from the blood of the fishes, the dark spots returned to view, partly but unmistakable. In twenty-four hours all traces of them had fully disappeared.

The dark catfishes retained in a black-walled vessel were, after an hour, still fully dark, nor were there any changes to be noted over the regions of injection of the extract or of the Ringer's solution. They were then put into a white-walled vessel where they slowly blanched. Seven hours after this transfer the three fishes were noticeably pale, but without evidence of dark spots. The next morning thirteen hours after the last record, all three were fully pale with faint but unquestionable dark areas over the regions injected with extract, but not over those injected with Ringer's solution. In a day dark areas on these fishes had disappeared. I had not enough crude extract to repeat these tests, but in consequence of their uniformity and definiteness, I think it fair to conclude that crude extract from pale smooth dogfishes contains a substance that darkens *Amerurus*.

The three pale and three dark frogs that were injected with pale dogfish extract and Ringer's solution yielded much the same results as the catfishes did. In all instances the extract produced a faint but unmistakable darkening of the calf of the pale frog and no noticeable

change in that of the dark frog. The dark reaction was by no means so pronounced as that in the catfish, but it was unmistakable. In all instances the injected Ringer's solutions was without effect on the tint of the calf. It is a surprising fact, but nevertheless a certain one, that the crude oily extract from a pale *Mustelus* which will produce a pale spot on another *Mustelus* will produce darkening in *Amerurus* and in the frog. It cannot of course be said that it is the same substance that produces these opposite effects, for the crude extract from the dogfish may contain one substance which blanches a dark dogfish and has no effect on the catfish and the frog and another which has no effect on the dogfish and yet darkens the catfish and the frog. Only future work can settle this question, but it is interesting that a single crude extract should excite these opposite effects.

## VI SUMMARY

1 The adult smooth-dogfish, *Mustelus canis*, when blinded, takes on a dark color. Blinded pups of this species are also dark irrespective of a white or a black illuminated environment.

2 Blinded pups in darkness are paler than blinded pups in the light. The darker tint of the pups in the light is due to a pituitary secretion, for it is replaced by full blanching when the pituitary gland is removed.

3 In blinded pups the pituitary gland does not discharge intermedin when these fishes are in the dark, it does discharge a very small amount when they are in the light. The receptor for this light response was not discovered.

4 Blanching in *Mustelus* can be artificially excited by adrenalin. There is no evidence that it is naturally excited by any blood-borne agent such as the W-substance hypothesized by Hogben. Blanching in *Mustelus* is due to a nerve-produced lipohumor, by a loss of intermedin from the blood, and by anoxemia.

5 The concentrating melanophore nerve fibers in *Mustelus* gave no evidence of antidromic response.

6 The crude concentrating lipohumoral extract from *Mustelus* after a year's retention in the dried state is still effective as a blanching agent for this dogfish. It induces darkening in *Amerurus* and *Rana*. This rather remarkable response may be due to another substance contained in the crude extract than that which caused the blanching of *Mustelus*.

## REFERENCES

- ABRAMOWITZ, A A 1936 Physiology of the melanophore system in the catfish, *Amenurus* *Biol Bull*, **71**, 259-281
- VON FRISCH, K 1912 Ueber das Parietalorgan der Fische als funktionierendes Organ *Sitzungsber Gesell Morph Physiol München*, **27**, 16-18
- GRIFFITHS, M 1936 The colour-changes of batoid fishes *Proc Linn Soc N S Wales*, **61**, 318-321
- HOGGEN, L 1936 The pigmentary effector system VII—The chromatic function in elasmobranch fishes *Proc Roy Soc London*, **B**, **120**, 142-158
- KROPP, B 1929 The melanophore activator of the eye *Proc Nat Acad Sci Washington*, **15**, 693-694
- LUNDSTROM, H M AND P BARD 1932 Hypophysial control of cutaneous pigmentation in an elasmobranch fish *Biol Bull*, **62**, 1-9
- PARKER, G H 1936a The electric stimulation of the chromatophoral nerve-fibers in the dogfish *Biol Bull*, **68**, 1-3
- PARKER, G H 1936b The chromatophoral neurohumors of the dogfish *Jour Gen Physiol*, **18**, 837-846
- PARKER, G H 1936c What are the resting and active states of chromatophores? *Proc Nat Acad Sci Washington*, **21**, 286-292
- PARKER, G H 1936a Color changes in elasmobranchs *Proc Nat Acad Sci Washington*, **22**, 55-60
- PARKER, G H 1936b Integumentary color changes in the newly-born dogfish, *Mustelus canis* *Biol Bull*, **70**, 1-7
- PARKER, G H 1936c The reactions of chromatophores as evidence for neurohumors *Cold Spring Harbor Symposia Quant Biol*, **4**, 358-370
- PARKER, G H 1936d The reactivation by cutting of severed melanophore nerves in the dogfish *Mustelus* *Biol. Bull.*, **71**, 255-258
- PARKER, G H 1936e Are there antidromic responses in the melanophore system? *Anat Rec*, **67**, Suppl 1, 37
- PARKER, G H 1937a Do melanophore nerves show antidromic responses? *Jour Gen Physiol* **20**, 851-858
- PARKER, G H 1937b Integumentary color changes of elasmobranch fishes especially of *Mustelus* *Proc Amer Phil Soc*, **77**, 223-247
- PARKER, G H 1938 The color changes in lizards particularly in *Phrynosoma* *Jour Exp Biol*, **15**, 48-73
- PARKER, G H, F A BROWN, JR., AND J M ODIORNE 1935 The relation of the eyes to chromatophoral activities *Proc Amer Acad Arts Sci*, **69**, 439-462
- PARKER, G H AND H PORTER 1934 The control of the dermal melanophores in elasmobranch fishes *Biol. Bull*, **66**, 30-37
- RODEWALD, W 1935 Die Wirkung des Lichtes auf die Hypophyse von *Rana temporaria* L *Zeitschr vergl Physiol.*, **21**, 767-800
- SCHAFFER, J G 1921 Beiträge zur Physiologie des Farbenwechsels der Fische I Untersuchungen an Pleuronectiden II Weitere Untersuchungen *Arch ges Physiol*, **188**, 25-48

- SCHARRER, E. 1928 Die Lichtempfindlichkeit blinder Elritzen (Untersuchungen über das Zwischenhirn der Fische I) *Zeit vergl Physiol*, **7**, 1-38
- VEIL, C AND R M MAY 1937 Hypophysectomie et changement de couleur chez la torpille (*Torpedo marmorata*) *C R Soc Biol Paris*, **124**, 917-920
- WARING, H 1936 Colour in the dogfish *Scyllium canicula* *Nature*, **138**, 1100
- WYKES, U 1936 Observations on pigmentary coördination in elasmobranchs *Jour Exp Biol*, **13**, 480-466
- YOUNG, J Z 1933 The autonomic nervous system of selachians *Quart Jour Micr Sci*, **75**, 571-624
- YOUNG, J Z 1935 The photoreceptors of lampreys II The functions of the pineal complex *Jour Exp Biol*, **12**, 254-270

### DESCRIPTION OF FIGURES

All figures except number 11 are photographs from the smooth dogfish *Mustelus canis* adults or pups. I am under obligation to Dr F M Carpenter for the preparation of these photographs.

#### PLATE 1

All figures on this plate are from melanophores on the dorsal side of the pectoral fins of dogfish pups.

Fig 1 Melanophores with fully dispersed pigment as seen in the dark phase of the dogfish.

Fig 2 Melanophores with fully concentrated pigment as seen in the pale phase of this fish.

Fig 3 Melanophores from a blinded dogfish in darkness. The pigment is more concentrated than in a similar fish in the light (Fig 4).

Fig 4 Melanophores from a blinded dogfish in light. The pigment is less concentrated than in a similar fish in darkness (Fig 3).

Fig 5 Melanophores from a hypophysectomized dogfish on an illuminated, black background.

Fig 6 Melanophores from a hypophysectomized dogfish on an illuminated white background. The pigment under the two conditions shown in Figures 5 and 6 is at full concentration, one condition is indistinguishable from the other.

#### PLATE 2

Fig 7 Dorsal view of a pup originally dark and divided by firm ligatures into three regions, anterior, posterior and central. The central region has been fully irrigated with Ringer's solution from the ventral aorta and has in consequence largely blanched while the anterior and posterior regions have remained dark.

Fig 8 Melanophores from the dorsal part of the head of the preparation shown in Fig 7. The pigment in these cells is about fully dispersed.

Fig 9 Melanophores from the dorsal part of the flank of the preparation shown in Fig 7. The pigment here is much concentrated.

Fig 10 Side view of the trunk of a dark pup next the anterior dorsal fin showing a pale spot induced by the injection of an extract from pale dogfishes' skins that had been kept dry in the laboratory for one year.

Fig 11 Side view of a pale catfish, *Amerurus nebulosus*, showing a dark spot under the anterior dorsal fin induced by an injection of the same kind of extract that produced a pale spot on a dogfish (Fig 10).



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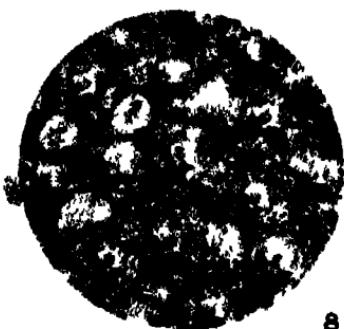


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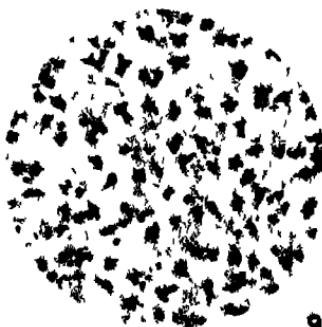




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THE HEAT CAPACITY AND PRESSURE VARIATION OF  
THE ENTHALPY FOR STEAM FROM 38° TO 125° C

PART V STEAM RESEARCH PROGRAM

By

SAMUEL C. COLLINS AND FREDERICK G. KEYES



Contribution from the Research Laboratory of Physical Chemistry,  
Massachusetts Institute of Technology, No. 398

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IN part IV of the present series of papers on steam properties volumes were recorded to temperatures as low as 195°. The measurements in part were made by the method of confining the steam with mercury, an excellent method provided the upper limit of temperature does not greatly exceed 300°. This restriction is due to the increasing failure with rising temperature of the Dalton rule of partial pressures which must be invoked in correcting for the pressure of mercury in the presence of the confined substances. At temperatures less than 195°, in the case of steam, its strong adsorptive properties probably account for the erratic and irreproducible quality of the results obtained. Earlier and similar experience with other substances led to a belief that the properties of gases at large volumes should be obtained by a method capable of supplying data free from adsorptive disturbances.

There are also other important reasons for developing an experimental procedure especially suitable for obtaining the low pressure properties of gases with high accuracy. Firstly, the statistical theory for low pressure gases is now well advanced and the application of the theory to highly precise data, were it available, could lead directly to exceedingly valuable quantitative information on the properties of the molecular field for pure gases and their mixtures. Secondly, the art of devising empirical analytical forms to correlate the smaller volume data could be based, as it should be, on a really accurate representation of the low (strictly zero) pressure behavior of the gas or gas mixture. In contrast to this the low pressure behavior of the gas is at present obtained of necessity from the correlative equation based on the high pressure data or what is much the same thing, by graphical extrapolation of the high pressure data to zero pressure. Without doubt the present general lack of appreciation of the poor

degree of correspondence of the van der Waals form of equation with the actual behavior of gases could not have persisted had exact low pressure data over a wide range of temperature been available a generation ago.

Work on the method we have attempted to develop was started some years ago (1932)<sup>1</sup> and has been carried through a number of stages, each involving in succession the incorporation in the apparatus of the means of attaining greater precision.

Fundamentally it is aimed to measure  $(\delta H/\delta p)_T$ , where  $H$  is the enthalpy ( $H = U + pV$ ),  $p$  the pressure, and  $T$  the Kelvin scale temperature, and also  $C_p$ , the heat capacity for constant pressure. The value of the first quantity for equation of state purposes lies in the fact that it is equivalent to the measure of  $\tau - T(\delta v/\delta T)_p$ , or preferably expressed  $\left(\frac{\delta \tau}{\delta T}\right)_p$  where  $\tau$  is the reciprocal absolute temperature. The quantity is zero for an ideal gas and likewise zero for a real gas at a series of pressures and temperatures the Joule-Thomson inversion points. For a van der Waals molecular model<sup>2</sup> for example, the quantity is equal to  $2a/RT - b$  for sufficiently high temperatures. Here  $a$  is proportional to the constant of the molecular attractive force and  $b$  to the molecular diameter. It will be clear on consideration therefore that the value of  $\left(\frac{\delta \tau}{\delta T}\right)_p$  is a direct measure of the departure of the gas from the ideal state and it may be used generally as a direct statistical measure of the resultant effect of the molecular forces. The thermodynamical equivalent of  $\left(\frac{\delta \tau}{\delta T}\right)_p$  is the negative of the product of the Joule-Thomson coefficient and the constant pressure heat capacity,  $-\mu C_p$ . By measuring  $\mu$ , or  $(dT/dp)_H$  as well as  $\left(\frac{\delta \tau}{\delta T}\right)_p$ , it is therefore possible to obtain  $C_p$ . In practice however it is not possible to measure these differential quantities but only certain

<sup>1</sup> F G Keyes and S C Collins, Proc Nat Acad Sci 18, 328 (1932). A Eucken, K Clusius, and W Berger, Zeit f Techn Phys. 13, 267 (1932) at about the same time published an account of work having for objective the measurement of the same quantity  $(\delta H/\delta p)_T$ , for air, while we were working with CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O. The methods, however, were different in detail in accordance with the descriptions given in the cited publications.

<sup>2</sup> Supposed to possess a positive potential infinite on contact of the molecular spheres of fixed diameter and a spherically symmetrical negative potential with distance index greater than four.

related average values, which through special interpretation may be used to deduce the derivatives<sup>3</sup>

In the earlier apparatus the gas was caused to flow at a steady rate through an isolated non-conducting capillary partially stopped with an electrical resistance heater. By adjusting the current in the heater it was possible to annul the cooling effect experienced by the gas through the fall of pressure in the capillary.<sup>4</sup> Operating however, without current in the capillary resistance heater gave a measure of the Joule-Thomson effect. This in principle is the method employed but the actual practice of the method, especially on low pressure gases, makes it necessary to introduce very complete and carefully controlled radiation screening and heat conduction control. We finally discarded all our earlier results on steam from glass apparatus and turned to the development of an all metal device. During the last year, however, a later all-metal apparatus has been constructed based on the full experience of the past six years for use with other gases and vapors. The results obtained with the first all-metal apparatus seem sufficiently consistent however, to induce belief in their value for extending or at least confirming our knowledge of steam properties at low temperatures.

#### THE APPARATUS

The design of the apparatus employed is represented in Fig. 1, drawn to scale. The whole equipment was submerged in an oil bath automatically maintained at constant temperature with variations not exceeding  $0.001^{\circ}$ . Steam entered an interchanger, 1, 2, consisting of a copper tube swaged down upon a twisted copper ribbon. The steam finally entered a low flow-resistance equalizer box, 3, consisting

<sup>3</sup>  $C_p$  may be defined as  $(\delta H/\delta T)_p$ .

<sup>4</sup> A Eucken, K Clusius, and W Berger, loc cit proceeded differently by allowing the gas to expand through an orifice producing thereby a Joule-Thomson cooling. The gas in its expanded but turbulent state was then returned to its initial temperature, as indicated by the thermocouples, by introducing electrical energy. The ratio of the measured electrical energy to the fall in pressure for a unit of the gas was taken as the measure of the isothermal change of the heat function with pressure. The suggestion that  $(\delta H/\delta p)_T$  be measured by using a heater embedded in the plug was made by Edgar Buckingham, Phil Mag 6, 519 (1903). We are indebted to Doctor Nathan S Osborne for calling the reference to our attention. Harvey N Davis (Phys Rev 5, 659, 1915) discussed fully the significance of data for  $(\delta H/\delta p)_T$  obtained according to Buckingham's suggestion. This important paper also contains a complete exposition of the various uses of Joule-Thomson data.

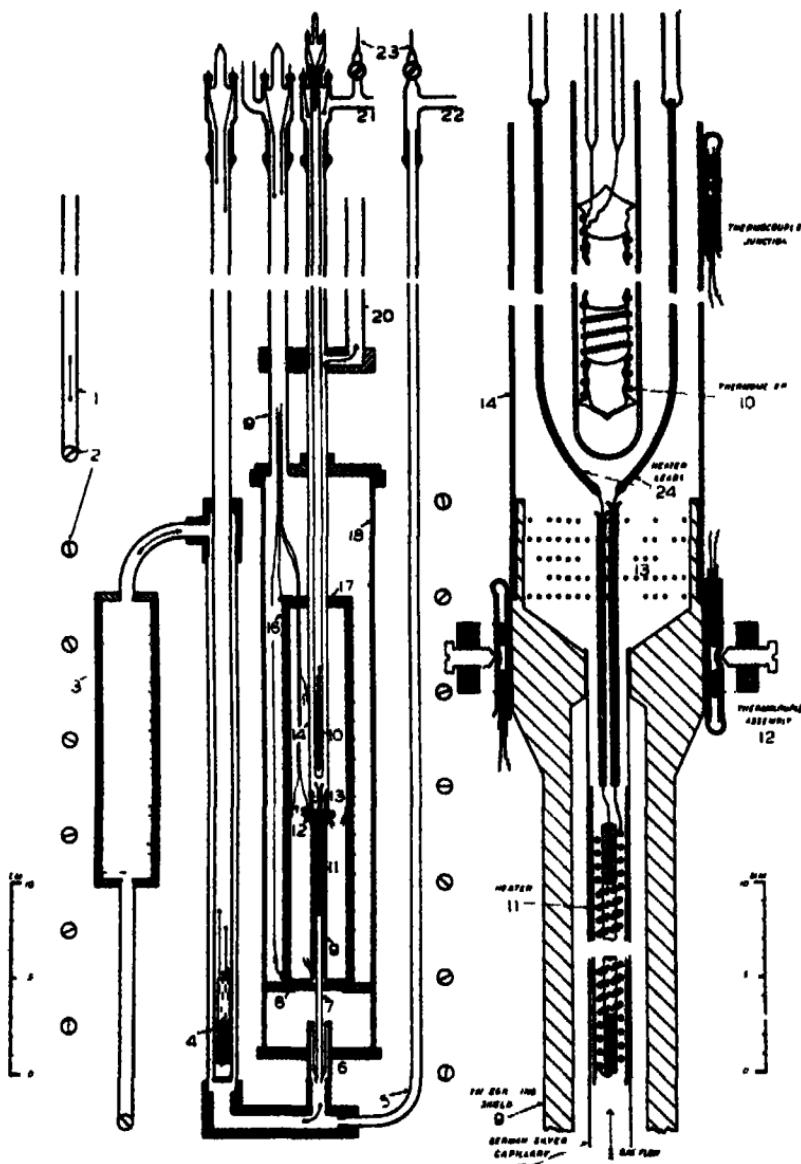


FIG. 1 Calorimeter and Enlarged View of Capillary

of a large number of gauze disks held in soldered contact with the walls of the container. On entering the calorimeter apparatus the steam temperature was registered on a platinum electrical resistance thermometer 4. The steam then entered the capillary 7, of 2 mm O.D. German silver having a wall thickness of 0.05 mm. The capillary was joined to a 10 mm O.D. German silver tube of 0.12 mm wall, 14, through the intermediary of a massive silver plated copper heat integrating shield, 9, bearing four-junction thermocouples the opposite junctions of which were fastened to the temperature controlled silver plated copper radiation shield 17. The steam passed over the capillary 240-ohm electrical resistance heater, 11, consisting of a No. 40 chromel wire wound in a fine helix and supported upon and within pyrex tubes. The copper plate 8, soldered to the vacuum case 18, prevents heat from being radiated from the heat guard 17 to the capillary 7. It also carries a thin sheet of mica which serves to keep the capillary centered. After passing the 50-mesh copper gauze system 13 designed to equalize the kinetic energy of the steam issuing from the capillary, the temperature is registered by thermometer 10. The steam passes to the condenser by means of tube 20 whilst the pressure on each side of the capillary is obtained through the use of tubes 21 and 22 leading to a mercury manometer.

The tubes 21 and 22 were at substantially room temperature and it was necessary to transmit the pressure of the steam without condensation. This was done by using air in the connecting tubes. During the period when the apparatus was being prepared for use, air was admitted slowly by means of stopcocks 23. The mixture of steam and air was allowed to stream through until the apparatus was about adjusted to begin observations. The cocks 23 were then closed and the air within the system was rapidly swept out leaving an air seal to the manometer which persisted for several hours.

After several attempts to generate steam at a steady rate, a heating element was constructed which floated upon the surface of the water in the generator. The device responded instantly to variations in the energy input a necessary condition for the satisfactory conduct of the measurements. Manual control of the generator energy input by the operator sufficed to maintain constancy of the pressure drop across the capillary to 0.01 mm for several hours. The steam admitted to the apparatus was of course superheated.

The effluent steam was condensed in a glass receiver maintained at zero by means of an ice bath. The inside surface of the receiver was treated with oil which produced a condition favoring condensation.

and the formation of water drops. The design of the condenser provided for a constant area of surface, an indispensable feature for accurate control of the effluent pressure.

The figure has been prepared to disclose the details of construction of the apparatus but brief comments about several items may be warranted. Thus the thermocouple attachment must provide good thermal contact and at the same time electrical isolation from the shield.<sup>9</sup> This compromise was accomplished by hard soldering the thermocouple junction to a copper tab.<sup>5</sup> The latter was then enclosed in a thin mica film held in a copper clip. There were four of these equally spaced around the shield and pressed thereon by means of steel watch screws supported in a metal collar as shown, 12, in the enlarged drawing at the right of the assembly.

The platinum wire, 0.1 mm diameter, for the resistance thermometers (28.5 ohms and 23.4 ohms) was machine wound upon a 0.25 mm steel piano wire in an evenly spaced spiral of 48 turns per cm.<sup>6</sup> A hollow glass form was then moulded in graphite of the form shown at 10 and used to support the platinum spiral previously released from the steel winding-wire through treatment in hydrochloric acid. The thermometer heads were joined to the metal tubes of the apparatus by means of de Khotinsky cement. The vigorously stirred constant temperature oil bath in which the apparatus was suspended was maintained at a fixed temperature to within better than 0.001° over the period of the observations.

From the construction of the apparatus it will be evident that it is possible to use the apparatus in two ways, and that it may even be used for gases which warm while experiencing a fall of pressure in the capillary (negative Joule-Thomson coefficient). The latter case is important since at temperatures sufficiently above the critical temperature of the gas-liquid phases all gases exhibit the negative Joule-Thomson effect which may be conceived of as due to the preponderating effect of the positive or "repulsive" molecular potential over the negative or "attractive" potential. Thus for a gas composed of the van der Waals model of the molecule, the Joule-Thomson effect is given for low pressures by the expression

$$(dT/dp)_H = \mu_0 = (2 a/RT - b)/C_p^{\circ}$$

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<sup>9</sup> We used essentially the same type of construction employed by Osborne, Stimson, and Fioch, Bur Stand J Res 5, 425 (1930) in their calorimeter.

<sup>5</sup> N. S. Osborne, H. F. Stimson, E. F. Fioch, and D. C. Ginnings, Bur Stand J Res 10, 165 (1933) used this compact coiled type of resistance thermometer. It is believed to have been first described by C. H. Meyers, Bur Stand J Res 8, 508 (1932).

where the van der Waals  $a$  is proportional to the molecular attractive force and  $b$ , to the repulsive force manifested on contact of the rigid molecular model spheres ( $b$  is four times the volume of the molecules)  $C_p^\circ$  is the heat capacity for zero pressure. Helium, for example, at ordinary temperatures is at such a high temperature relative to its critical temperature that the effect of the repulsive potential preponderates and it is now known<sup>7</sup> that " $b$ " is actually not a constant but a temperature function a fact substantiated long ago through the viscosity-temperature<sup>8</sup> behavior of helium. There is enough additional evidence available, similar in kind, to lead to the belief that the behavior characteristic of helium is a general property of all gases although for many, experimental demonstration by known procedures is practically impossible because of the limitation<sup>9</sup> of materials at high temperatures.<sup>9</sup>

#### MODE OF CONDUCTING THE MEASUREMENTS

The mode of operation of the apparatus used was based largely on the ease with which the results obtained could be interpreted. It is perceived that the quantities to be derived from the measurements,  $C_p$  and  $(\delta H/\delta p)_T$ , are each a function of temperature and pressure. The former quantity may, however, be partially expressed in terms of the latter as follows:

$$C_p = C_p^\circ + \frac{\delta}{\delta T} \int_0^p \left( \frac{\delta H}{\delta p} \right)_T dp \quad (1)$$

It becomes evident therefore that measurements should be made to obtain the energy required to return the expanded fluid to its temperature prior to experiencing the pressure drop  $\Delta p$ . To interpret such data it is convenient to start with a general expression for the enthalpy,  $H$ , as follows:

$$H = \int_{T_0}^T C_p^\circ dT + \psi_0 p + \psi_1 p^2 + \dots + h \quad (2)$$

<sup>7</sup> J. R. Roebuck and H. Osterberg, Phys Rev 43, 60 (1933). Joule-Thomson data are given from 83° to 573° K and it is shown that for low pressures the effect is negative throughout the temperature range with a maximum at roughly 423° K.

<sup>8</sup> Frederick G. Keyes, Zeit f. Phys Chem., Cohen Festband, 1927, p 709, also, Chem. Rev 6, 175 (1929).

<sup>9</sup> Steam above 3000° C at low pressure, it is estimated, would exhibit Joule-Thomson properties similar to helium but at these temperatures water could not, of course, preserve its identity nor could apparatus be devised from known materials for measurements.

where the coefficients<sup>10</sup> of the  $p$  (pressure) terms are pure temperature functions of the form  $\psi_0 = \left(\frac{\partial B_0\tau}{\partial \tau}\right)$ ,  $\psi_1 = \left(\frac{\partial \varphi_1\tau}{\partial \tau}\right)$  following from the assumption that for low pressures the pressure of a unit of steam is given by the equation

$$p = \frac{RT}{r - B} \quad (3)$$

where  $B = B_0 + \varphi_1 p + \dots$

It is important for ease of interpretation to have several measurements available at increasing pressure drops for the case of exact temperature restoration. In the more general case we have from (2)

$$H_f - H_i = \int_{T_i}^{T_f} C_p^\circ dT + \psi_0 p_f - \psi_0 p_i + \psi_1 p_f^2 - \psi_1 p_i^2 + \dots \quad (4)$$

where subscripts  $i$  and  $f$  refer to the initial and final states of the gas.

The above equation for restored temperature experiments,  $T_f = T_i$ , becomes however

$$[H_f - H_i] = -\psi_0(p_i - p_f) - \psi_1(p_i^2 - p_f^2) \quad \text{at } T_f = T_i \quad (5)$$

and when data are accumulated at a series of fixed temperatures,  $\psi_0$ ,  $\psi_1$ , etc become known in relation to temperature. With this information it becomes possible to deduce the quantity  $\int_{T_i}^{T_f} C_p^\circ dT$

from measurements in which greater amounts of energy, Equation 4, were introduced than required for temperature restoration, ( $T_f > T_i$ ). In the case of steam the measurements were all conducted at initial pressures below an atmosphere where coefficients other than  $\psi_0$  and  $\psi_1$  were not required. The Table I gives a summary of the measurements taken with the apparatus of figure 1.

The saturation pressure at 38.94°C is less than 55 mm and at 60°C, 149.38 mm. The difficulty of making accurate measurements at these low pressures is considerable in view of the necessity of maintaining a large enough drop to secure accuracy in the measurement of the energy. The rates of flow also become large because of the larger volumes with attendant kinetic effects. The number of measurements at the two lower temperatures were on this account less than at the higher temperatures where the larger available pressure range made possible more favorable conditions for the measurements.

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<sup>10</sup> F G Keyes, L B Smith, and H T Gerry, Proc Am Acad Arts and Sci, 70, 341 (1936).

When the details of the measurements became available it was found that a correction of the order of one percent was required in all the measurements. The circumstances making correction necessary are as follows. The figure 1 shows that the copper integrating shield 9 telescopes into the German silver tube 14 to the extent of about 6 mm, the end being located 8 mm above the capillary exit. The effluent steam had a linear velocity varying from 1000 to 5000 cm per second. The temperature of shield 9 assumed the temperature of the outgoing steam as indicated by thermometer 10 during the measurements of  $(\Delta H/\Delta p)_T$ , and also the temperature of thermometer 10 in the measurements for ascertaining  $C_p$ .° Taking the former type of measurements for detailed consideration it will be clear that in the circumstances the heater 11 will supply the heat required to compensate for the Joule-Thomson cooling,  $\int_{p_i}^{p_f} (\delta H/\delta p)_T dp$ , and also a part of the heat corresponding to the mean kinetic energy acquired by the gas in the course of its turbulent passage through the capillary. Immediately after issuing from the capillary the kinetic energy begins to be dissipated with attendant rise in temperature. Had the telescoping portion of shield 9 and the gauze baffle in contact therewith been long enough, the heat corresponding to the acquired kinetic energy of motion of the steam would have been given to the shield. Since a steady state of flow is maintained, a condition would have ultimately resulted, assuming perfect thermal contact of the heater and thermometer leads with the heat guard 17, whereby exact heat compensation would have been attained and the heat supplied by the heater would have been only that corresponding to the quantity

$$\int_{p_i}^{p_f} (\delta H/\delta p)_T dp$$

A second factor was the imperfect thermal contact of the heater and thermometer leads with the heat guard 17. The effect of the rise in temperature of the effluent steam at the baffle was therefore to cause loss of heat along the heater and thermometer leads. It is evident that the imperfect thermal contact was more serious in its effect in the measurements where the temperature as indicated by thermometer 10 was considerably greater than the temperature of the bath or as given by thermometer 4.

In order to come to a clearer understanding of the effects referred to, measurements of the temperature effects manifested by a gas after changing linear velocity were carried out with air, carbon dioxide,

ammonia, and hydrogen. The gases were caused to flow in an insulated 10 mm glass tube having a short section of 2 mm tube. The temperature effect,  $\delta t$  (corrected of course for the Joule-Thomson effect) proved to be directly proportional to the pressure drop per unit length of the pressure restraining tube or  $\delta t \sim \frac{\Delta p}{\Delta l}$  and independent, as would be expected, of the nature of the gas.<sup>11</sup> In addition, one junction of a thermocouple was fixed to tube 14 above thermometer 10

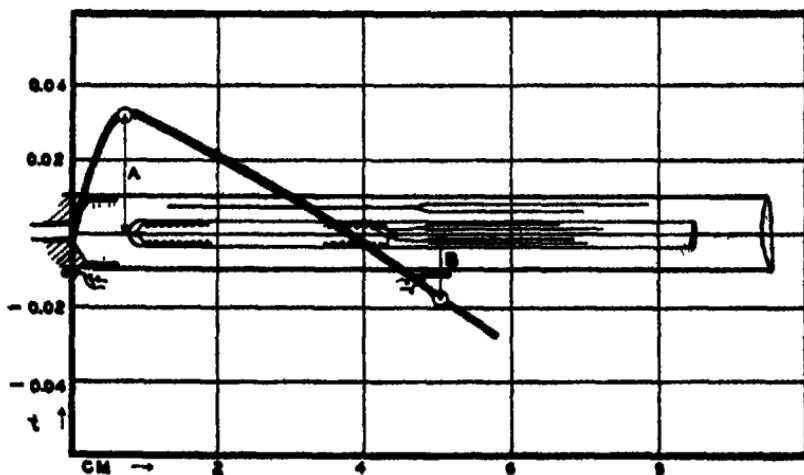


FIG. 2 Variation of Temperature with Distance along Tube 14

and the other junction to the shield 9 for the purpose of observing similar kinetic temperature effects in steam. At high rates of flow the thermal leakage along the leads was small enough to give a reasonably good measure of the kinetic effects.

Figure 2 is a representation of the temperature along tube 14 from the exit of the capillary past the thermometer 10. The magnitude of  $\delta t$  deduced from the separate flow measurements is given by the empirical relation  $\delta t = 0.055 \left( \frac{V}{86} \right)^2$  where  $V$  is the volume of steam leaving the capillary per minute. The values of  $\delta t$  in the diagram correspond to the fifth entry at 100° given in table I. The value of

<sup>11</sup> An interesting account of a wide variety of experiments on the temperature effects for moving gases is given by J. P. Joule in the second volume of the Collected Works, beginning on p. 215.

$\delta t$  at  $B$  is that measured by a thermocouple junction whose other junction is on shield 9. The temperature at  $B$  relative to the capillary end may be either positive or negative in sign for any specific measurement, depending on the conditions of flow velocity and heat input by the heater 11. The resistance thermometer actually measures a mean temperature over its length, but from the relative positions of the thermometer 10 and the thermocouple at  $B$  it was deduced that the temperature correction to be applied to the resistance thermometer was 2/5ths of the difference between the temperature at  $A$  and at  $B$ . The whole correction was of the order of  $0.002^\circ$  for low rates of flow and  $0.05^\circ$  for the highest.

### DISCUSSION OF THE RESULTS

The first stage in treating the corrected data given in Table I was to evaluate  $\psi_0$  and  $\psi_1$  as defined by equation (5). It will be noted that at temperatures 38.94 and 59.44 only one constant temperature value of  $(\Delta H / \Delta p)_T$  is available and it is accordingly not possible to determine

empirically the quantity as a linear function of pressure. At 80.02, 100, and  $125^\circ$  C, however, the pressure range from the saturation condition to the lowest operable pressures was sufficient to give the pressure dependence of  $\psi$  with pressure.<sup>12</sup> It will be observed, however, that in no case is the final temperature exactly equal to the initial temperature. The worst case is measurement 6 at  $100^\circ$  where  $T_f - T_i$  is 0.0763. In this as in every other instance the values of  $C_p$ ,<sup>o</sup> by A. R. Gordon<sup>13</sup> as corrected by E. Bright Wilson, Jr.<sup>14</sup> were used to compute the "correction" required to reduce the actual experimental values to the values that would have resulted had  $T_f$  been exactly equal to  $T_i$ . In the worst case, the sixth measurement at  $100^\circ$ , the value of  $C_p$ ,<sup>o</sup>  $\times 0.0763$  amounted to one in forty of  $(H_f - H_i)$ .

From the data of the  $(\Delta H / \Delta p)_T$  measurements at 80.02, 100 and  $125^\circ$ , values were deduced for  $\psi_0$  and  $\psi_1$ . The similar data for 38.94 and  $59.44^\circ$  C were reduced by using  $\psi_1$  values computed from the equation of state for steam. The values are listed in Table II.

<sup>12</sup> It is inferred that the assumption of linear dependence of  $(\delta H / \delta p)_T$  on pressure is sufficiently exact within the limits of precision of the present measurements on the basis of the higher temperature volume data (No. IV of the present series of papers).

<sup>13</sup> A. R. Gordon, J. Chem. Phys. 2, 65 (1934).

<sup>14</sup> E. Bright Wilson, Jr., J. Chem. Phys. 4, 526 (1936). The amount per mol of steam to be added to Gordon's values is  $4.08^{-3} RT$ , or about a part in 380 for the mean temperature of the experimental range of the present paper.

The values of  $\psi_0$  were smoothed by least square solution of the data for the differences between the observed and equation of state  $\psi_0$  values. It will be noted that  $\Delta\psi_0$  becomes negligibly small at high temperatures. Thus at  $200^\circ$   $\Delta\psi$  is 0.0432 I, while at  $300^\circ$  it is 0.0043 I.

The quantity  $\Delta\psi_0$  may be integrated on the assumption that  $\Delta B_0$  of the equation of state is zero for  $\tau = 0$ . Thus we find

$$B_{0 \text{ obs}} - B_{0 \text{ cal}} = 0.419 \tau^{12} 10^{36} - 0.0550 \tau^{24} 10^{36} \quad (6)$$

This leads to a value of  $B_{0 \text{ obs}}$  4.1 cc./g. greater than the corresponding  $B_0$  used in the equation of state at  $38.94^\circ$ <sup>15</sup>. The error this would cause in computing the saturation volumes would, however, amount to only one in six thousand. It does not appear that the volumes of steam below  $200^\circ$  would be seriously modified by the introduction of the new  $B_0$  information provided a part in several thousand is an error of small consequence.

It will be observed from Table II that the  $\psi_1$ 's deduced at the three highest temperatures are of the same order of magnitude as those given by the equation of state. The precision with which  $\psi_1$  can be determined depends, however, upon the range of variation of the pressure drop across the capillary heater which is necessarily very restricted at  $125^\circ$  and lower. It is our opinion that the values of  $\psi_1$  "observed" may be in error by twenty percent in the  $80$  to  $125^\circ$  range and probably by a greater amount at the two lower temperatures. For many calculations at low pressures only the  $B_0$  values are required.

### THE $C_p$ VALUES

The reduction of the remaining data where  $t_i$  exceeded  $t_f$  was next carried out using the observed  $\psi_0$  and  $\psi_1$  values. The latter quantities correspond of course to the temperatures of the gas entering the calorimeter in the  $t_i = t_f$  experiments. The reduction of the heat capacity data requires in addition, however, values of the  $\psi$  coefficients for the higher temperature given by thermometer 10. The expressions given at the bottom of Table I were used to compute the desired values of  $\psi_1$  and  $\Delta\psi_0$  was used to obtain the "smoothed" difference ( $\psi_{0f} - \psi_{0i}$ ). This difference was then applied to the observed or unsmoothed value of  $\psi_{0i}$  to obtain  $\psi_{0f}$  obs used in the computations of

<sup>15</sup> The formulation of the equation of state as given in paper No. IV was guided in the neighborhood of  $60$  to  $100^\circ$  by a knowledge of preliminary  $\psi_0$  values obtained from an investigation using glass apparatus which preceded the use of the present improved all-metal construction of Fig. 1.

$C_p^\circ$ . For temperatures 38.94 and 59.44 the  $\psi_1$  data from the equation of state were used. The part played by the  $\psi_1$  terms at these latter temperatures was of the order of 2 percent. Table II gives the values obtained for  $C_p^\circ$ .

The values of  $C_p^\circ$  in Table II have been entered in the diagram Figure 3, along with a full line representing the Gordon-Wilson<sup>16</sup>

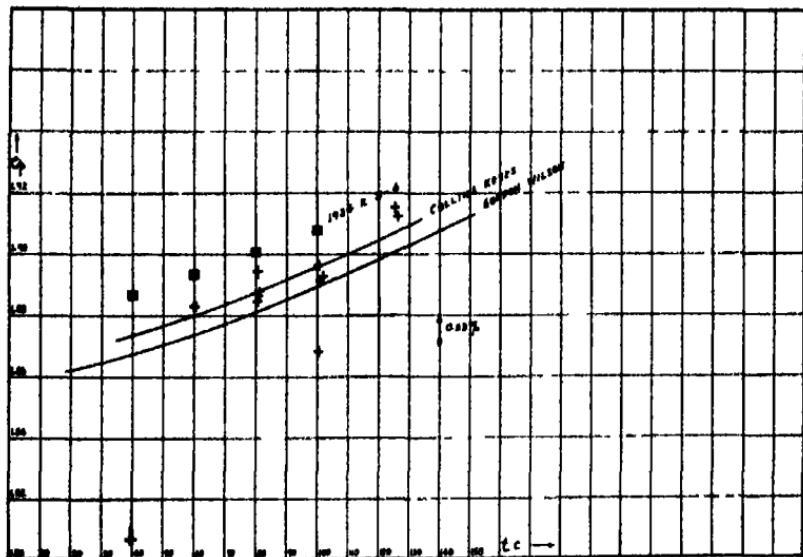


FIG. 3 Plot of Experimental Data for the Specific Heat of Steam with Computed Values.

computed values. The "Collns-Keyes" line is drawn from the empirical equation

$$C_p^\circ = 1.47825 + 7.745 \cdot 10^{-4} + \frac{47.8365}{T} \quad (7)$$

wherein the coefficients of  $T$  and  $T^{-1}$  are the same, as used to represent the G-W values. The "C-K" line is about one in three hundred above the G-W line for  $C_p^\circ$  versus temperature.

The value of  $C_p^\circ$  from the single measurement at  $t_f$ , 39.41°C is

<sup>16</sup> The curve is drawn from the equation representing the Gordon values of  $C_p^\circ$  which is Eq. 22 of paper No. IV, obtained by Professor J. H. Keenan to which the E. Bright Wilson, Jr. term  $4.08 \cdot 10^{-4} RT$  has been added.

3.3 percent low relative to the smoothed value. The measurement was made at an initial pressure of 50.26 mm with a final pressure of 8.78 mm, the pressure difference amounting to 41.48 mm. The control apparatus allowed a steady state to within about  $\pm 0.01$  mm but small variations in pressure are more disturbing at lower pressures.<sup>17</sup> Moreover the velocity effects already referred to are more pronounced at the lower pressures. It is regrettable that more measurements are not available at the lower temperatures but in the absence of apparatus improvements indicated in the course of the present work, additional measurements would not have been profitable.

The role of  $C_p^\circ$  in the formulation of the equation for the enthalpy,  $H$ , is fundamental and in the equation 15A for steam<sup>18</sup> the A. R. Gordon values were used. Allowance for the rotational distortion of the water molecule, made by E. Bright Wilson, Jr., increased the A. R. Gordon values by  $4.08 \cdot 10^{-4} RT$  while the new experimental data suggests still larger values to the extent of a part in three hundred. This is an amount of the same order as the precision of the present measurements of  $C_p^\circ$  which may accordingly be regarded as furnishing direct experimental evidence of the validity of Wilson's calculation, were confirmation necessary. Accepting the G-W values for  $C_p^\circ$ , the steam enthalpy equation 15A of paper IV must be corrected by the addition of the term  $9.4 \cdot 10^{-4} (T^2 - 273.16^2)$ .<sup>19</sup> Some of the con-

<sup>17</sup>A sudden change in pressure in the course of a measurement causes a temperature disturbance given approximately by the relation  $\Delta T = - [R \psi_1^\circ V_p \Delta p] / \rho$ , which indicates that  $\Delta T$  will be large as the pressure is small.

<sup>18</sup> Proc Am Acad Arts and Sci 70, 344 (1936)—Paper IV.

<sup>19</sup>The new values of  $\psi_0$  would only affect the values of  $H$  below 100° to a slight extent, but account must be taken of the fact that the present experiments give no reliable measure of  $\psi_1$ . The equation of state extrapolated value of  $\psi_1^{100}$  is 0.979 I.; while  $\psi_2$  is 0.003, an entirely negligible quantity in the present state of our knowledge of steam properties. The following statement suggests a way of determining  $\psi_1$ .

The measured value of the heat of evaporation (2256.6 I.) is probably known to a part in five thousand through the measurements of Osborne, Stimson, Floch, and Ginnings working at the National Bureau of Standards. By using the Clapeyron equation and the known highly exact values of  $dp/dT$  along with the liquid volume at 100°, we may arrive at a quite precise value of the 100° saturation specific volume of steam, namely 1673.34 (equation of state gives 1673.3). Comparing this with the ideal-gas value for the volume at 100° and at atmosphere pressure, we obtain the gas defect amounting to  $B = -26.61$  cc which may be represented by  $B = B^\circ + \psi_1 p$ . The value of  $B^\circ$  and  $\psi_1$  from the equation of state are -25.07 and 1.593 respectively. The  $B^\circ$  deduced from the present investigation is however -24.51 cc/g so that

sequences arising from a comparison of these modified enthalpy values with existing experimental data are of interest.

There already exists a large body of measurements of the enthalpy, specific heat, and Joule-Thomson numbers for steam over wide ranges of pressure and of temperature, and further enthalpy data obtained by our colleagues in the program of steam investigation will be forthcoming in the near future. Further intercomparison of the data is therefore not profitable at this time. The comparisons that have been made, however, indicate that the values of enthalpy computed on the basis of the Gordon  $C_p^{\circ}$  values and the equation of state are in very good agreement with, (a) the saturation enthalpy measurements of Osborne, Stimson, Fioch, and Ginnings, excluding computed values at saturation above about  $340^{\circ}$  where the equation of state is invalid, (b) the enthalpies from Havlíček and Miskovsky<sup>40</sup> measurements over the superheat region to  $550^{\circ}$  to about a part in five hundred (the computed values, however, tend to be larger), (c) the latent heat measurements of Henning, Jakob, Jakob and Fritz, (d) the Knoblauch and Koch, and recent Koch heat capacity measurements, particularly the latter's recent measurements, and (e) the Harvard Joule-Thomson values by Davis and Kleinschmidt.

By way of summary it may be stated that while the measurements here presented confirm the Gordon-Wilson  $C_p^{\circ}$  values and provide more reliable  $\phi_0$  values, it is believed premature to reformulate the enthalpy equation in view of the excellent agreement with the published measurements. At a later time a comprehensive reduction of all available data using the G-W  $C_p^{\circ}$  values<sup>41</sup> may disclose a consistent trend indicating whether or not the equation of state is a sufficiently precise representation of the volume data.

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we are led to the value  $-21$  for  $\varphi_1$  at  $100^{\circ}$ . In a reformulation of the equation of state in its present form, it would be necessary to make the  $\varphi_1$  equation pass through this value along with similarly derived values from latent heats below  $100^{\circ}$ . We will not attempt this formulation at the moment since modern values for the latent heat are not yet available below  $50^{\circ}$ .

<sup>40</sup> Helv Phys Acta, 9, 161 (1936).

<sup>41</sup> In the August number of the Physical Review (1937) infra-red data for steam (rotation-vibration bands to  $J = 11$ ) are reported by H M Randall, D M Dennison, Nathan Ginsburg, and Louis R Weber. Further information on the moments of inertia of the molecule is also promised by the authors.

TABLE I  
EXPERIMENTAL DATA FOR LOW PRESSURE STEAM

<i>t</i> °C	<i>P<sub>t</sub></i> Atm	<i>P<sub>f</sub></i> Atm	( <i>P<sub>t</sub></i> - <i>P<sub>f</sub></i> ) Atm	( <i>T<sub>f</sub></i> - <i>T<sub>t</sub></i> ) °	( <i>H<sub>f</sub></i> - <i>H<sub>t</sub></i> ) Joules/gram	Rate of flow Gram/sec.
38 94	0 06404	0 00786	0 05618	0 0142	1 68977	0 001255
	0 06613	0 01155	0 05458	0 9484	3 33999	0 001291
59 44	0 17736	0 00784	0 16952	0 0021	3 65592	0 005495
	0 17898	0 01228	0 16670	0 9668	5 42080	0 005311
	0 18040	0 01251	0 16789	1 6850	6 80378	0 005409
80 02	0 18087	0 01246	0 16842	0 0028	2 63888	0 005110
	0 18272	0 01280	0 17012	1 5554	5 61078	0 005189
	0 30942	0 01926	0 29016	0 0100	4 64590	0 010514
	0 31016	0 01926	0 29090	1 1224	6 75823	0 010548
	0 31088	0 01843	0 29245	2 0280	8 40656	0 010567
	0 31042	0 01774	0 29268	2 0014	8 45166	0 010611
100 00	0 18125	0 01148	0 16977	0 0051	2 05506	0 004819
	0 18173	0 01227	0 16945	1 1899	4 29753	0 004824
	0 26455	0 01587	0 24888	0 0291	3 06378	0 008103
	0 26564	0 01614	0 24950	1 7408	6 31702	0 008120
	0 26494	0 01574	0 24920	4 1370	10 85447	0 008057
	0 48150	0 02731	0 45418	0 0763	5 72909	0 017621
	0 48672	0 02689	0 45983	1 7271	8 92784	0 017802
125 00	0 18988	0 01153	0 17835	0 0033	1 61055	0 004781
	0 18963	0 01145	0 17818	1 6436	4 75247	0 004752
	0 19451	0 01157	0 18294	3 2307	7 82712	0 004911
	0 29198	0 01613	0 27585	0 0218	2 45406	0 008654
	0 29583	0 01731	0 27852	0 0496	2 60916	0 008689

TABLE II  
ENTHALPY COEFFICIENTS

	Smoothed - $\psi_{\text{obs}}$	Obs - $\psi_0 \text{I}_J$	Eq St - $\psi_1 \text{I}_J$	Obs - $\psi_1 \text{I}_J$	Eq St - $\psi_1 \text{I}_J$
38 94	29 08	28 869*	33 581		10 395
59 44	20 48	20 774*	23 050		4 150
80 02	15 266	15 195	16 616	2 283	1 910
100 00	11 852	11 871	12 574	0 832	0 979
125 00	8 931	8 916	9 269	0 395	0 461

\* Deduced from experimental data using  $\psi_1$  from equation of state. Equation for  $\psi_1 = [-0.9906r^2 \cdot 10^{14} + 1.318r^{14} \cdot 10^{16} - 1.1732r^{24} \cdot 10^{16}] \text{ I}_J$

\*\*  $\Delta\psi_0 = \psi_0^{\text{obs}} - \psi_0^{\text{eq st}} = [5.45r^{12} \cdot 10^{16} - 1.373r^{24} \cdot 10^{16}] \text{ I}_J$

TABLE III  
COMPUTED VALUES OF  $C_p^{\circ}$  FOR STEAM I J PER GRAM

$T_i$	38.94	59.44	80.02	100.00	125.00
	1 8068 (39.41)				
		1 8828 (59.92)	1 8827 (60.28)		
			1 8845 (80.58)	1 8943 (80.80)	1 8879 (81.02)
				1 8924 (102.07)	1 8865 (81.03)
					1 8963 (100.50)
					1 8915 (100.87)
					1 9121 (126.02)
					1 9151 (125.82)

The numbers in brackets represent the average temperature



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**THE FOUR MAGNETIC TRANSVERSE EFFECTS IN COPPER  
AND THEIR CHANGES WITH TEMPERATURE  
NEW MEASUREMENTS**

**By EDWIN H HALL**



# THE FOUR MAGNETIC TRANSVERSE EFFECTS IN COPPER AND THEIR CHANGES WITH TEMPERATURE NEW MEASUREMENTS

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THESE effects, which are found in metals generally, have all been known for some fifty or more years, but because of their commercial unimportance they are unfamiliar to the general scientific public and even to most physicists. They are, however, of considerable interest to those who strive to form a satisfactory theory of electric and thermal conduction in metals.

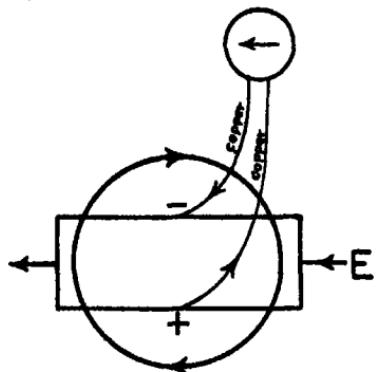
Their characters and the sign conventions which have become attached to them are illustrated in Figures 1 to 4. The rectangle in each figure represents a plate of metal through which flows, in the direction of the arrow-heads, either a current of electricity,  $E$  in (1) and (2), or a current of heat,  $H$  in (3) and (4). In each figure the metal plate is subjected to a magnetic field of force the direction of which is indicated by the directions of the arrows on the large circle, the circle representing a winding of the coil of the electromagnet.

In Figure 1 the magnetic field produces and maintains a difference of electrical potential at points exactly opposite each other on the long edges of the rectangle, and if two such points are placed in circuit with a galvanometer a current of electricity passes through it. Reversal of the magnetic field reverses the transverse potential-gradient in the plate and so reverses the direction of the current through the galvanometer. This is the Hall effect.

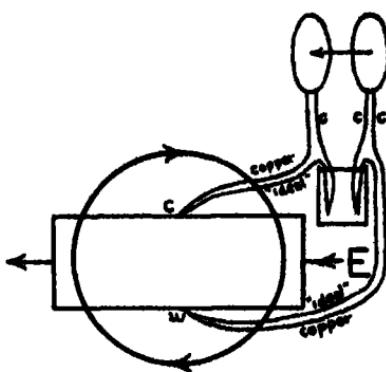
But the same conditions which give this effect set up a transverse temperature-gradient, the direction of which depends on the direction of the magnetic field. This is the Ettingshausen effect. It can be detected and measured by attaching a thermo-electric junction at a point on the upper edge of the plate and a similar junction at the opposite point on the lower edge of the plate, each of these junctions being part of its own thermo-electric circuit including a galvanometer coil. See Figure 2.

In Figures 3 and 4, illustrating the Nernst and the Righi-Leduc effects, respectively, the galvanometer connections are omitted.

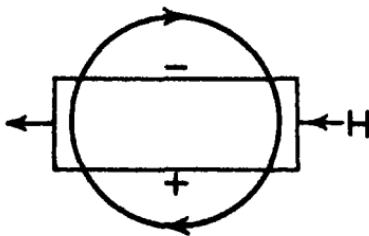
During the last few years I have given much attention and physical labor to the problem of getting reasonably accurate measurements of these four transverse effects in copper at various temperatures ranging



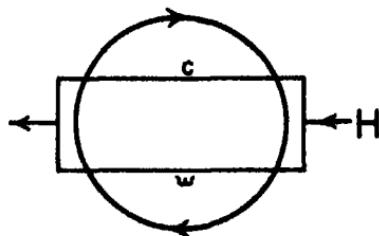
**FIG 1**  
**HALL EFFECT**  
 $R$  or  $eT_h$   
**POSITIVE**



**FIG 2**  
**ETTINGHAUSEN EFFECT**  
 $P$  or  $eT_h$   
**POSITIVE**



**FIG 3**  
**NERNST EFFECT**  
 $Q$  or  $eT_s$   
**POSITIVE**



**FIG 4**  
**LEDUC EFFECT**  
 $S$  or  $eT_h$   
**POSITIVE**

**FIG 1-4** Diagram defining the four transverse effects

from about  $20^\circ \text{C}$  to about  $90^\circ$  I have used the same general method which I used and described years ago,<sup>1</sup> but with many changes of detail

<sup>1</sup> *Physical Review*, vol 26, (1925), pp 820-840

I have worked with copper for various reasons. It is easily obtained in a state of high purity, its general electrical and thermal properties, with which the transverse effects must be coordinated in any satisfactory theory of conduction, are well known, it presents compara-

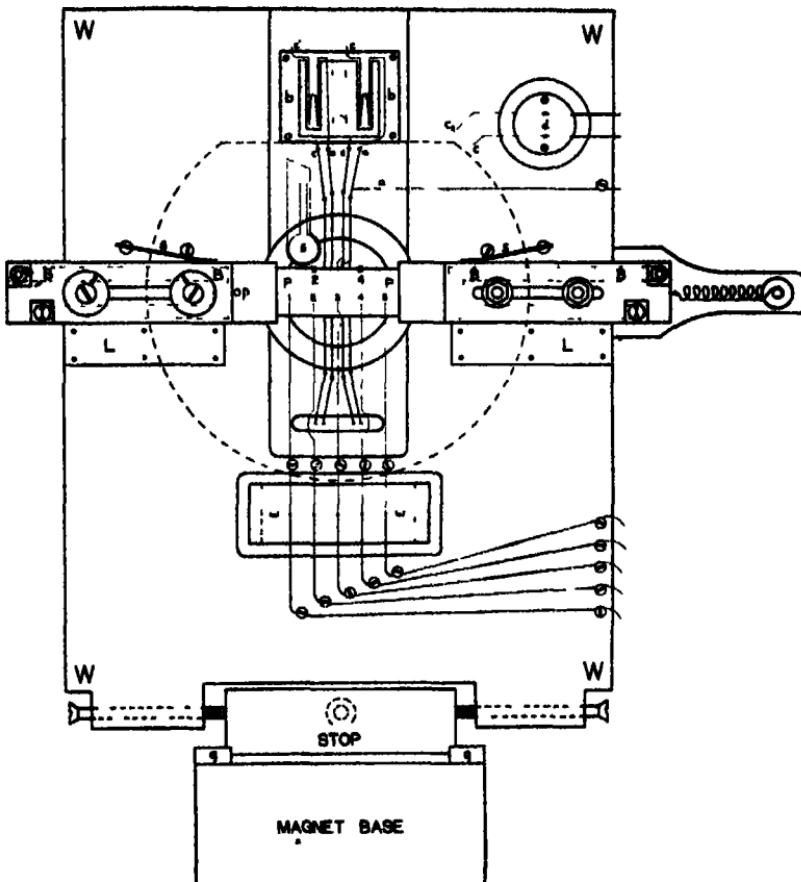


FIG. 5 General view of the mounting and connections of the plate

tively simply thermo-electric conditions, because at certain vital points copper-to-copper connections can be used. It is true that the effects in question are smaller in copper than in some other metals, but I have worked with the encouraging reflection that a method of measurement found satisfactory with copper would work even better with other metals.

My aim has been to measure the four effects with an accuracy of one per cent at each of three temperatures, and though I have probably fallen somewhat short of this mark, especially with the Ettingshausen effect, I feel that I have obtained results worth publishing and have developed a method worth describing in some detail.

As before, I have used for my study a piece of metal, *PP* in Figure 5, about 5 cm long, in the clear, between brass blocks, *BB* and *BB'*, to which it is soldered at the ends, and 2 cm wide. But, whereas in previous measurements with non-magnetic metals I have used strips about 0.011 cm thick, the thickness of this piece of copper is about 0.097 cm.

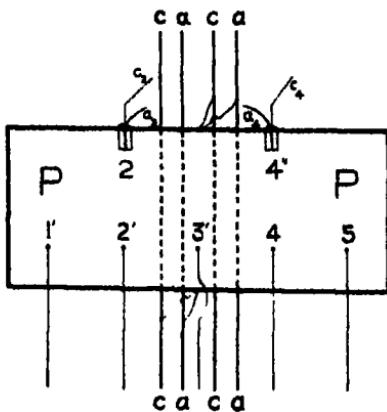


FIG. 5a. Details of the wire connections of the plate.

This increase of thickness, made practicable for my experiments by the use of improved apparatus, electromagnet and galvanometer, has brought many advantages. First, there is less danger of distortion of the plate under the stresses to which it is subjected. Second, uncertainty as to the effective width of the plate is greatly reduced by the fact that the junctions (shown but not lettered at the mid-points of the upper and lower edges, respectively, of the plate *PP* in Figure 5 and 5a) by means of which the various transverse effects are measured, are now made on the thickness dimension of the plate, whereas they were previously made near the edge of the width dimension and so encroached upon and practically reduced this width. Third, errors due to uncertainty regarding temperature gradients within the plate, as affected by interchange of heat between the plate and its surroundings, are lessened nearly in proportion as the thickness is increased.

## MOUNTING AND CONNECTIONS OF THE COPPER PLATE

The manner in which the plate, with its attachments, is mounted and held must be described in some detail. It is essential that the plate shall not change position appreciably upon reversal of the magnetic field, which in the Hall and the Ettingshausen effects exerts a "ponderomotive" force of about 600 grams tending to push the plate upward or downward across the lines of the field. But opportunity must be given for the plate to expand in length without bending, when it is heated.

In Figure 5, *W W W W* is a board, a common small drawing-board, re-enforced at the back of its mid-part to a total thickness of about 2.5 cm by a disk of ply-wood screwed on. A circular hole 6.4 cm in diameter is cut through this board and across this hole the plate *PP* is held by the supporting, water-channeled, brass blocks *BB* and *BB*. One pole piece is shown extending into the hole behind the plate. Each of the blocks *BB* rests upon a ledge *L* of wood about 0.3 cm thick and each is bolted to the board. But, in order to allow free longitudinal expansion of the plate during heating, the nuts on the bolts of the right-hand *BB* are left slightly loose, and a spiral spring, attached to the outer end of this *BB*, is intended to overcome the friction of this block on its support during the expansion of *PP* (This spring is not needed when *PP* is of copper, but may be of use when a softer metal, silver or gold, is used.) To keep the movable *BB* pressed securely against the ledge *L* when the direction of the "ponderomotive" force of the field is upward, a spring *S* pushes down upon *BB*. The left-hand *BB* is bolted tightly to the board, split washers being used under the bolt-heads, but for greater security a down-pressing spring acts upon it also. A pin, *p*, reaching through the thinned end of this *BB* and into the board, is useful in preventing lateral movement of this block when its bolts are loose.

To prevent the supporting board *W W W W* from rocking or turning on the magnet pole, two screws at the bottom of the board are used as Figure 5 indicates, bearing against a stop carried on the magnet base between two guides *g* and *q*.

The technique of making the many soldered connections of the plate *PP* is perhaps worth describing. First, the connections with the blocks *BB*.

Examination of Figure 6, which is a horizontal section through *PP*, *BB*, *BB*, and the pole-pieces of the magnet, will show that one face of *PP*, the rear one in Figure 5, is in the same plane with the corresponding surfaces of the blocks *BB* and with one surface of the board, the

one shown in Figure 5. To make the soldering now in question the blocks are placed upon a brass plate, so fashioned that they can be held upon it properly aligned and spaced to receive *PP*, with the surfaces where the soldered joints are to be made facing upward

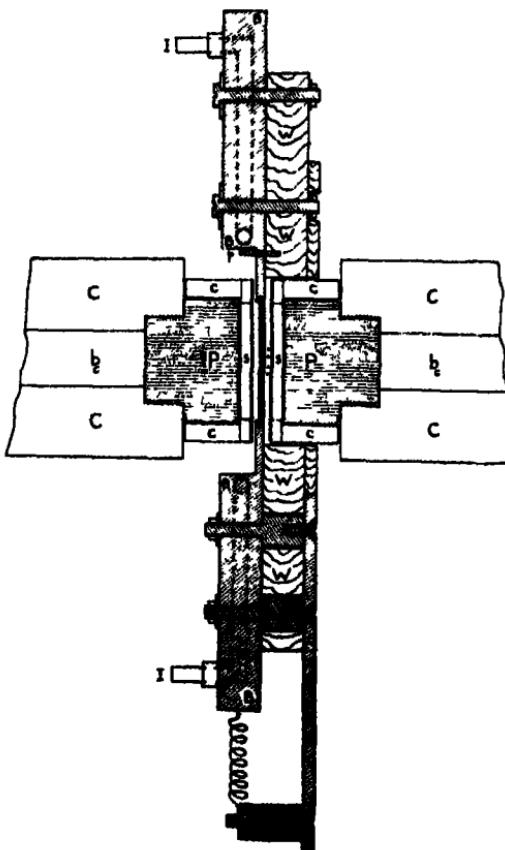


FIG. 6 Horizontal cross section through the middle of the plate and the surrounding apparatus

These surfaces and the corresponding parts of *PP* are "tinned" with solder and the plate is put in position on the blocks, the length of the lap at each end being about 0.3 cm

Then a block of brass, about 5 cm tall and of such a base as to cover *PP* almost completely but leave a little uncovered area at

each end, is placed upon  $PP$ . This block is now heated by a flame, which does not touch  $PP$ , till the "tinning" solder beneath each end of the plate is melted and flows under the weight of the block. A little more solder is now fed in where it seems to be needed at each junction and the whole affair is then allowed to cool, the block remaining in place. During the whole of this operation one of the blocks  $BB$  is bolted firmly to the supporting brass plate but the other one must have freedom to move slightly, lengthwise, to allow for the longitudinal expansion and contraction of  $PP$  during heating and cooling. A current of steam flowing through the channels of the blocks  $BB$ , and through a channeled block of brass placed under  $PP$ , helps in this soldering process.

The fine-wire connections of the plate, though indicated in Figure 5, are seen to better advantage in the larger-scaled Figure 5a. At the mid-point of the upper edge of  $PP$  is soldered a thermo-electric junction consisting of a no. 36 copper wire and a no. 36 constantan wire, twisted together. This junction is made by a method illustrated in Figure 7 of my paper in the Physical Review for December, 1925, and it is soldered within itself before it is attached to the plate. The method of attachment is this. The brass plate carrying  $PP$  and the blocks  $BB$  is placed and secured in such a way that the plane of  $PP$  is vertical and its longer edges are horizontal. A small soldering-iron, mounted in such a way that it can move in a vertical plane only, is so adjusted that its tip, filed to a rectangle about 0.1 cm. long, corresponding to the thickness of the plate, and 0.05 cm. wide, can be brought quickly and squarely down upon the upper edge of  $PP$  at the point where the copper-alloy junction is to be attached. A bit of soldering flux having been placed on this point, the soldering iron, carrying a little solder at its tip and strongly heated, is turned quickly on its bearing till its tip rests for an instant on the designated spot of the plate and is then lifted. If everything has gone well, a little mound of solder will be left firmly adhering to the plate at the desired spot.

With a thin-edged file a narrow valley is cut through this mound in the direction of the thickness of the plate. In this valley, or groove, the copper-alloy twisted junction is laid. The process of making this junction has left four wires extending from it, two from each end, several centimeters long. By a proper use of these wires the junction can be held in place in the groove described while another descent of the heated soldering iron fuses the solder about it and makes a neat, firm attachment. The two wires leading from one end of the twisted

junction are now cut off, the two at the other end being left for making contacts with the galvanometer circuit.

These contacts are made by way of the straight no 28 wires which Figure 5a shows as passing under  $PP$  in the direction of its width, vertically. The one of these wires that lies farthest to the right,  $aa$ , is of constantan alloy, the one next it, marked  $cc$ , is of copper. The no 36 alloy wire from the junction on the upper edge of  $PP$ , left about 1 cm long, is soldered at its outer end to the right-hand no 28 alloy wire. The no 36 copper wire from the junction, left also about 1 cm long, is soldered at its outer end to the no 28 copper wire.

The no 28 wires are held in position, and are kept reasonably straight during the expansion of heating, by soldering them, above  $PP$ , to the heads of small brads or screws driven into the board and, below  $PP$ , to the ends of bent springs, consisting of phosphor-bronze strips which reach (see Figure 5) through a slot in the board. These springs start from the rear surface of the board, they exert a steady pull upon the wires.

The no 28 copper wire to which the no 36 copper wire of the junction on the upper edge of  $PP$  is connected leads off, through an all-copper path, to one set of coils in a differential galvanometer. The corresponding no 28 alloy wire is soldered at its upper end to a finer wire of the same alloy, and this finer wire runs to the top of a brass block,  $bb$  in Figure 5 descends nearly to the bottom of a cylindrical chamber therein, then turns upward and at mid-height of the chamber meets a fine copper wire, to which it is soldered. This makes the second, or outer, junction of the thermo-electric couple which has its other junction on the upper edge of  $PP$ . The fine copper wire,  $c'$ , leading from the chambered junction, connects with an all-copper line reaching to the set of galvanometer coils already referred to. The thermo-electric circuit thus completed I shall call the upper circuit, because it starts from the junction on the upper edge of  $PP$ .

A similar thermo-electric circuit, starting with the copper-alloy junction on the lower edge of  $PP$  and having its other junction in another chamber of  $bb$ , includes a different set of galvanometer coils. This will be called the lower circuit. Connections are made in such a way that warming the junction on the upper edge of  $PP$  and cooling the junction on the lower edge cooperate to produce a movement of the galvanometer index.

The brass block  $bb$ , in the chambers of which the outer junctions are placed, is channeled for the flow of water, to control its temperature, the same stream of water that passes through one of the pole-caps

presently to be described. The chambers in *bb* are lined with rather thick paper, partly for electric insulation and partly to minimize fluctuations in the junction temperatures due to short-time fluctuations in the temperature of the water stream. Each chamber is closed at the top by a hard-rubber plug in which the wires entering the chamber are held.

In work at the higher temperatures no effort is made to raise the temperature of the electromagnet, which remains not very different from that of the laboratory room. It is, however, important to have the immediate surroundings of the plate *PP* as nearly as may be equal to the mean temperature of the plate itself. Accordingly each pole-piece of the magnet is covered by a close-fitting metal cap channelled for the flow of temperature-controlled water. The cap is, as its name would indicate, closed at one end, and in this end a disk of stainless steel, about 0.4 cm thick and in diameter equal to the pole-piece, is held between two thin plates of brass.<sup>1</sup> See *s* and *s'* in Figures 6 and 7. The water stream enters the cylindrical part of the cap radially near the open end, runs along a grooved channel, parallel to the axis of the cylinder, till it reaches the cylindrical surface of the steel disk, there divides into two streams which run in opposite directions for 180° circumferentially around the disk and then reunite, going out as a single stream by a channel similar to the entering one. See Figure 7 which shows a vertical section parallel to lines of the magnetic field.

The cap is thermally insulated from the pole-piece which it covers. The water runs downward through each pole-cap and before reaching the southern one, the right-hand one in Figure 7, it passes through the block *bb*, of Figure 5, which, as already told, contains within its chambers the outer junctions of the upper and lower thermo-electric circuits. The external diameter of the pole-caps is slightly less than the diameter of the hole cut in the board behind *PP* (Figure 5), so that the southern cap projects into this hole and its flat end is about 0.25 cm distant from the plate.

The water stream which runs through the northern pole-cap, the left-hand one in Figure 7, runs later through a brass block, *b'b'*, beneath which, on a thin wooden bridge, lie the junctions where no. 36 alloy wires leading from the points 1', 2', 3', 4', 5' on *PP* (see Figure 5)

<sup>1</sup> The use of the stainless steel disk is to make the gap of non-magnetic material between the pole-pieces shorter than it would be if the pole-caps were made entirely of brass. If the pole-caps are made entirely of steel, they tend to slide off the pole-pieces when the magnetic field operates.

are soldered to no. 28 alloy wires. These junctions are insulated from the block  $b'b'$  by a thin sheet of mica. Block  $b'b'$  is not shown in Figure

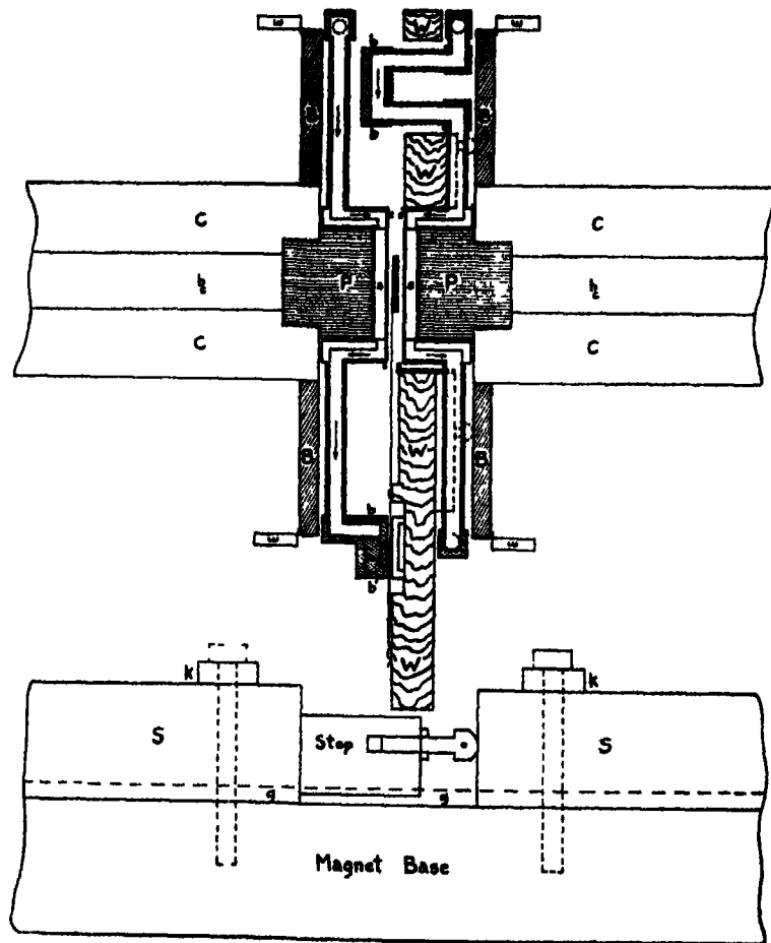


FIG. 7 Vertical cross section through the middle of the plate and the surrounding apparatus

5, but the positions of its ends are there indicated by dotted lines running across  $ww$ , which is the wooden bridge already mentioned. A cross-section of this bridge is shown facing  $b'b'$  in Figure 7, and one of the wire junctions lying between is there indicated

The object of this meticulous arrangement is to control the temperature of the junctions mentioned and to keep them all at very nearly the same temperature, even when the direction of the longitudinal heat flow through  $PP$  is reversed. For these junctions lie in the thermo-electric circuits by means of which the longitudinal temperature gradient along  $PP$  is measured during the study of the Nernst and the Righi-Ledue effects. Different sizes of the same kind of alloy usually have a considerable difference of thermo-electric quality. If we can keep all the junctions just mentioned at the same temperature, and if the junctions of the no. 28 alloy wires with the copper wires, to which they must be joined somewhere on the line to the galvanometer, can be kept at one temperature, we at least approximate the desired condition of things. This condition is that the only thermo-electric forces operative will be those which lie in the couple consisting of two of the no. 36 alloy wires soldered to the plate  $PP$ , for example those at points 1' and 2' (Figure 5), and the part of the copper  $PP$  which lies between these points. The junctions of the no. 28 alloy wires with copper wires lie in a thermostated oil-bath kept a little above the temperature of the room.

The points 1', 2', etc., lie at 1 cm intervals, nearly, along a line about halfway between the lower edge and the middle line of  $PP$ . The temperature gradient along the 1' to 5' line is probably more nearly the average gradient for the whole width of the plate than the gradient along the middle line or that along an edge would be.

At each of the points 2'' and 4'' on  $PP$ , best seen in Figure 5a, is a twisted and soldered junction of no. 36 copper and no. 36 alloy wire, but these junctions are not soldered to  $PP$ . Each rests on a thin flake of mica cemented to  $PP$  by means of glyptol, and each is cemented to the mica beneath it in the same way, the glyptol being well baked on by hours of heating well above 100° C. The wires  $a_2$  and  $a_4$  leading from these junctions meet each other in a soldered joint, not shown in Figure 5a, about 1 cm above the upper edge of  $PP$ . The wires  $c_2$  and  $c_4$  leading from the junctions run, by lines not shown in the Figures, to connect with the similarly marked copper wires projecting to the left from beneath the brass disk,  $d$ , shown in the upper right-hand corner of Figure 5. Behind  $d$ , as the dotted lines indicate, the fine copper wires  $c_2$  and  $c_4$  are joined to heavier copper wires, which lead off to the galvanometer. Under, or behind, these junctions is another, equally large, brass disk fastened to the board, which is there cut away to a depth of about 0.3 cm, the thickness of the disk. The junctions are electrically insulated from the disks by thin sheets of

mica. The object of this arrangement is to keep the two junctions very nearly at the same temperature with each other, though this temperature may change somewhat with change of direction of the heat-flow in  $PP$ .

The junctions 2" and 4", which are about 2 cm apart, are of great use in measurements of the Ettingshausen effect, for, though no longitudinal temperature-gradient along  $PP$  is needed or desired in such measurements, an appreciable one is likely to exist because of the Peltier effect produced by the passage of the strong longitudinal electric current (see Figures 2 and 5) from brass to copper at one end of  $PP$  and from copper to brass at the other end. This accidental longitudinal temperature-gradient is very troublesome, because it produces a Righi-Leduc effect (see Figure 4) which combines with the Ettingshausen effect and may be equal to many per cent of the latter. It is not practicable to measure this disturbing temperature-gradient by means of the junctions 1' to 5' on  $PP$  and then eliminate the Righi-Leduc factor by calculation, for the longitudinal electric current which is flowing along the plate precludes the use of these junctions for thermo-electric measurements.

Nor is it practicable to measure accurately the longitudinal temperature-gradient by means of the junctions 2" and 4", for it cannot be safely assumed that either of these junctions has the same temperature as the part of  $PP$  over which it lies. It cannot even be safely assumed that the temperature gradient indicated by use of the junctions 2" and 4" bears a constant ratio to the true gradient when this gradient is changed in magnitude or direction. The best that we can do is to try, by controlling the temperatures of the water streams passing through the right-hand and the left-hand blocks  $BB$ , respectively, to keep the temperature gradient along  $PP$  constant in magnitude and direction during reversal of the direction of flow of the electric current along  $PP$ .

The indications given by the junctions 2" and 4" may enable us to do this, though they cannot tell us just how great this gradient is. If we can keep this constancy of temperature gradient along  $PP$ , we can, by combining the apparent Ettingshausen effect observed when the electric current runs east along the plate with the apparent Ettingshausen effect observed when the electric current runs west along the plate, eliminate the Righi-Leduc error from our final Ettingshausen value. But this operation must, to be successful, be conducted with very great care. A temperature gradient of  $0.1^\circ$  per cm., will make a difference of perhaps 20% in the apparent value of

the Ettinghausen effect. This explains the need of such detailed precautions as those I have been describing. Even different pieces of commercially pure copper wire will show disturbing differences of thermo-electric quality under the conditions here dealt with.

The temperature-equalizing disks *d* (Figure 5) are a recent feature of my arrangements. It was not used in my study of the Ettinghausen effect in copper.

The *s* in Figure 5 is a slip of bakelite carrying a single turn of fine copper wire which can be made part of one of the thermo-electric circuits, in order to minimize the induction throw of the galvanometer index when the magnetic-field circuit is made or broken while the galvanometer circuits are closed. As a rule, however, I make a practice of breaking the galvanometer connections before closing or opening the magnet circuit.

#### THE ELECTRO-MAGNET

*BB* and *BB* in Figure 7 are brass plates at the ends of the magnet coils. The windings of these coils are of bare copper strip of rectangular cross-section,  $\frac{3}{4}$  inch by  $\frac{3}{16}$  inch, suitably insulated from each other. Two of these windings are indicated by the rectangles *w* and *w* of Figure 7. *CC* and *CC* in the same Figure are the soft iron cores ("ARMCO") of the coils, 8.1 cm in diameter. Through each core runs a cylindrical hole, *b<sub>c</sub>*, in which is placed a close-fitting brass tube.

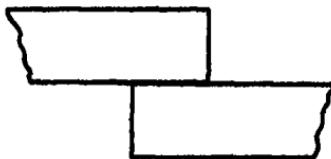


FIG. 8. Figure showing a brazed junction of two copper strips of the magnet coil.

carrying a stream of cold water, the object of which is to keep the temperature of the cores from rising too far. This temperature was usually a few degrees above that of the room.

The process of winding the coils presented a mechanical problem which was solved as follows. Two copper strips, each 5.64 m long, were brazed together at one end in the manner indicated by Figure 8. One of these strips was wound in one direction and the other in the opposite direction, with thin insulating material between, on a thin insulating hoop just large enough to slip easily on the core of the magnet. This gave a "pan-cake" coil two turns wide, or long, and

twelve turns deep. The complete coil for each core consists of five such "pan-cakes" connected to each other in series. The length of copper strip in each coil is about 56.4 m., and the resistance of the two coils in series is about 0.04 ohm.

By the test coil and ballistic-galvanometer method data were found for plotting a curve showing the relation between intensity of the magnetic field and strength of the magnetizing current.

#### THE TEMPERATURE-CONTROLLED WATER-STREAMS

These water-streams, to which reference has been made, come from three thermostated tanks, each of about 11 liters capacity, which stand on a shelf some feet higher than the electromagnet. On a lower shelf there is beneath each tank a rotary pump which takes water from that tank, sends it through some channel of the apparatus carried by the board *WWWW*, in Figure 5, and back into the tank. The water-stream from one tank divides after passing through its pump, thus furnishing two streams for the two magnet pole-caps. One of the other tanks sends a stream through the right-hand, the other through the left-hand, BB in Figure 5.

To prevent trouble from electric leakage by way of the water-circuits care is taken to have a considerable length of the stream in each circuit run through a rubber tube. Frequent measurements of insulating resistances between circuits requiring insulation from each other showed numbers running from 500,000 ohms upward.

#### THE DIFFERENTIAL GALVANOMETER

The galvanometer used for measurement of the transverse effects is mechanically much like the one described by Nichols and Williams in Vol. 27 (1908) of the Physical Review, but is different in its mode of winding. The coils have the form of two pairs of truncated cones, or frustums, an upper pair and a lower pair, corresponding to the upper and the lower set of needles of the astatic suspended system. The bases of each pair face each other. Each frustum is wound double, so that it really consists of two independent, but interpenetrating, coils almost identical in shape and size. Thus there are in all eight independent coils, and for each such coil there are two independent binding posts. This arrangement makes possible a considerable variety of combinations, with a resistance varying from about 0.5 to about 30 ohms. In particular it lends itself to differential use, such as is needed in measurement of the Ettingshausen effect and the Right-Leduc effect.

The galvanometer is enclosed by four cylindrical soft-iron shields, having a total thickness of about 3.5 cm. A much greater total thickness would be needed to protect the instrument completely from disturbing magnetic forces.

The sensitivity of such a galvanometer is much affected by change of temperature, and to lessen trouble from this cause the instrument is enclosed in a wooden closet containing a device for thermostating the air.

In spite of these control arrangements the sensitivity of the instrument may change several per cent within a few hours, and it must therefore be measured frequently.

#### THE THERMO-ELECTRIC COUPLES

These were of commercial copper wire against "Advance," a variety of constantan furnished by the Driver-Harris Company. Tests of these couples which I made with the temperature intervals 0° C to 50° C and 0° to 100° showed that I could with sufficient accuracy for my purpose use the tables for copper-constantan published by L. H. Adams (*Jour Amer Chem Soc*, vol 36', 1914, pp 68-69), provided I applied to his temperature intervals giving 0.0001 volt a constant factor. This factor is 1.008 when I use my no. 36 constantan, as I do at the most vital points, but is about 1.07 for my no. 32 constantan and about 1.05 for my no. 28 constantan, against copper in all cases. This indicates that a couple made of my no. 36 constantan against my no. 32 constantan would have an e.m.f. about 6 per cent as large as that of a copper-constantan couple.

Two couples made of my no. 36 constantan against copper agreed very closely with each other.

#### MEASUREMENT OF THE TRANSVERSE EFFECTS

Some of my measurements on copper were made as early as 1933, but I had great difficulty with the Ettingshausen effect and in 1935, remembering that Professor Noel Little of Bowdoin College had found<sup>1</sup> that in a non-uniform magnetic field there may be air currents due to the magnetic quality of oxygen, I decided to enclose my electromagnet in a vacuum-chamber, or at least one of greatly reduced air pressure. As the walls of this chamber are for the most part of steel about one quarter of an inch thick, this change required remeasurements of the strength of the field between the poles of the magnet, as a function of the strength of magnetizing current. It was found, however, that the steel shell affected the magnetic field but little.

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<sup>1</sup> *Physical Review*, vol 2 (1927), p 901

I have since this change, worked as a rule with an air-pressure of about one two-hundredth of an atmosphere within the chamber. This should reduce the heat-convection influence of the air currents to a negligible value. But, as I shall show in discussing the Righi-Leduc effect measurements, the use of this device has made little, if any, difference in the effects observed. It was well to try it, but I doubt whether I shall use it much hereafter. One disadvantage in its use is that, if any rubber tubes carrying hot water, or even heated hard-rubber plugs, lie within the vacuum-box, sulphur given off from them attacks the copper wires exposed to it. A coating of some kind (I have used glyptol) is needed to protect them, and the copper plate also was protected in the same way.

On account of the bad appearance of some of the fine-wire connections on the plate, all of these connections were renewed, with new wires, about the first of September 1936. The end connections of the plate with the blocks *BB* were renewed at the same time. Especial precautions were taken at that time to protect the wires. In December, 1936, the two most vital junctions, those at the upper and the lower edge of the copper plate, were replaced once more. In January, 1937, the rubber tubes previously used within the vacuum-box were replaced by copper tubes.

*The Hall Effect.* I shall give details only for the observations made in 1937. The first column in the Table 1 gives the date of the work. *A*, is the strength, in amperes, of the longitudinal current through the plate, put in the *W* column when this current ran *west* and in the *E* column when it ran *east* through the plate. *H* is the strength of the magnetic field in gauss. *E* is the fraction of a volt required to produce a deflection of 1 cm. on the scale of the galvanometer through the resistance, about 400 ohms, of the Hall effect circuit. *T* is the temperature of the mid-point of the upper edge of the plate, determined by means of a copper-constantan couple, one junction of which was attached to the plate at the point mentioned while the other was in a thermostated water-tank the temperature of which was not many degrees different from that of the plate. It is assumed that *T* gives nearly enough, within a few tenths of a degree, the temperature of the middle cross-section of the plate. *R* is the Hall effect coefficient as measured, before a certain correction, presently to be discussed, is applied.

These observations seem to indicate a slight increase in the value of *R* with rise of temperature.

Seven other measurements, each involving a *W* and an *E* direction

TABLE 1

Date	(W)	$A_s$ (E)	H	$E \times 10^4$	T	$R \times 10^4$
Feb 26, '37	129 1		11370	1 423	22 7°}	-4 98}
Feb 26, '37		130 2	11440	1 442	22 6°}	-5 00}
Feb 20, '37	128 2		11310	1 463	57 1°}	-5 10}
Feb 20, '37		129 9	11400	1 451	57 1°}	-4 98}
Feb 12, '37	128 9		11320	1 276	91 4°}	-5 09}
Feb 12, '37		128 5	11250	1 258	91 4°}	-5 08}

of  $A_s$ , ranging in time from August, 1933, to October, 1935, with values of  $T$  varying from 27.5° to 22.4°, gave values of  $R \times 10^4$  between limits -5.01 and -4.90, the means being, for  $T$ , 24.0°, and for  $R \times 10^4$ , -4.954.

Four other measurements, the first in October, 1933, and the last in January, 1934, gave the following means for  $T$ , 53.9°, and for  $R \times 10^4$ , -4.952.

Eight other measurements, the first in November, 1933, and the last in February, 1934, gave, as means,  $T$  = 91.4° and  $R \times 10^4$  = -4.965.

It is to be remembered that between the date of the last measurements referred to in the three preceding paragraphs and that of the first of those recorded in Table 1 all the connections of the copper plate, including the end connections, were renewed. It is probable that the conditions of the later measurements were somewhat better than those of the earlier ones, but I shall give them all equal weight in estimating the values of  $R$  at the various temperatures. Combining them I get the following mean values

TABLE 2

Temperature	$R \times 10^4$
23.8°, or 24°	-4.959, or -4.96
54.5°	-4.970, or -4.97
91.4°, or 91.5°	-4.977, or -4.98

There is still a trace of evidence indicating that  $R$  increases slightly with rise of temperature, but not enough to make sure.

Of the various corrections discussed at some length in my paper of 1925, already referred to, the only one that seems to be called for here as applicable to the Hall effect in copper is that, called correction (b), which takes account of the limited width of the magnetic field and the limited length of the copper plate exposed to that field. My previous estimate of this correction was 8%, additive, and though the greater thickness of the plate now used may suggest some reduction of this estimate I shall use it here, getting the amended and final figures

TABLE 3

Temperature	$R \times 10^4$
24°	-5 36
54 5°	-5 37
91 5°	-5 38

The fact that correction (b) is of about the same per cent magnitude for all of the transverse effects reduces the importance of exactness in the estimation of this correction. That is, an error here will leave nearly unaffected the ratios of the various effects.

*The Ettingshausen Effect.* This, as I have already indicated, is by far the most difficult of the four to measure, partly because it is small and still more because it is usually accompanied by an accidental Righi-Leduc effect. The device by which I sought to eliminate error due to this cause from the mean value of  $P$  given by any "pair" of observation series, one made with the plate current running west and the other with the current running east, has been described in the discussion of junctions 2" and 4" shown in Figures 5 and 5a. When my observations with these junctions indicated that the longitudinal temperature-gradient in  $PP$  was not appreciably the same for both directions of  $A_s$ , I made by calculation the usually small correction that seemed to be called for.

Whatever degree of accuracy I finally attained in my study of the Ettingshausen effect, I have good reason for rejecting all of my earlier measurements, and I shall use none of those made before January 18, 1937. The value of  $A_s$  in the later measurements was about 128.5 amperes, that of  $H$  about 11,300 gauss, that of  $E$ , the e.m.f. required to produce a galvanometer deflection of 1 cm through the resistance of an Ettingshausen circuit, about  $6 \times 10^{-8}$  volt.

In Table 4 the direction of flow of the  $A_s$  is indicated by the letter  $W$  or  $E$ . It is to be noted that the individual values of  $P$  in a  $W$  and  $E$  "pair" may differ widely, because of the Righi-Leduc disturbance, without greatly affecting their mean.

The data of this Table show a decided increase of the Ettingshausen effect with rise of temperature, but the three mean values of  $P$ , when plotted against the temperatures, would not fall upon a straight line. They would do so if the value found at 56.7° were increased about 1.4 per cent, or the values found at 22.5° and 91.4°, respectively, decreased by corresponding amounts. I have no warrant for making such changes and must let the figures stand as they are, though I feel no assurance that the  $P-T$  line is a curve of the form here indicated.

TABLE 4

Date	<i>A.</i>	<i>T</i>	<i>P</i> × 10 <sup>8</sup>	Date	<i>A.</i>	<i>T</i>	<i>P</i> × 10 <sup>8</sup>
1/18	W	22 1	-1 531	1/20	W	56 6	-1 442
1/19	E	22 1	-1 152	1/21	L	56 2	-1 384
2/1	W	22 7	-1 391	1/29	W	56 8	-1 356
2/2	E	22 7	-1 296	1/30	E	56 6	-1 453
2/3	E	22 7	-1 296	2/6	W	57 0	-1 391
2/4	W	22 8	-1 298	2/8	E	56 5	-1 524
2/23	W	22 8	-1 357	2/18	W	57 1	-1 548
2/24	E	22 5	-1 304	2/19	L	57 0	-1 439
— — — —				— — — —			
22 5°				56 7°			
$\pm$				$\pm$			
0 007				0 008			
Date	<i>A.</i>	<i>T</i>	<i>P</i> × 10 <sup>8</sup>	Date	<i>A.</i>	<i>T</i>	<i>P</i> × 10 <sup>8</sup>
1/22	W	91 4	-1 656	1/26	E	91 1	-1 414
1/26	E	91 1	-1 414	1/27	L	91 2	-1 586
1/27	L	91 2	-1 586	1/28	W	90 8	-1 571
1/28	W	90 8	-1 571	2/10	E	91 4	-1 616
2/10	E	91 4	-1 616	2/11	W	91 4	-1 603
2/11	W	91 4	-1 603	2/16	W	91 2	-1 633
2/16	W	91 2	-1 633	2/17	L	91 3	-1 496
— — — —				— — — —			
91 4°				-1 570			
$\pm$				$\pm$			
0 010							

The "probable error" of each of the three mean values found for *P* is less than 1 per cent of the value, but there may, of course, be errors which the magnitude of the "probable error" does not hint at.

As to corrections of the kind discussed in my 1925 paper, one, (b), already applied to the observed Hall effect values of the present paper, is called for here, an increase of 8 per cent in the observed values of *P*. Of the others, the only one that appears to need consideration is (f), which is defined by the following quotation from my earlier paper: "My view of the matter is that the Ettinghausen effect or the Righ-Ledue effect is all the time tending to increase the transverse temperature-difference and that the heat conductivity of the plate, assisted by the conductivity of the packing lying between the plate and the pole pieces, tends to reduce it. What we measure is the compromise result of these tendencies. We are now concerned with the question how much greater this difference would be if, other things being equal, the packing were thoroughly non-conductive for heat."

An approximate estimate for this correction can be found thus. Let  $\alpha$  in Figure 9 represent a section of the copper plate lying between two vertical planes parallel to the axis of the magnet and 0.1 cm apart. Let  $P$  and  $P'$  represent the opposed faces of the pole-caps, the space between  $\alpha$  and either  $P$ , 0.25 cm wide, being occupied by the cotton packing. Let the top end of  $\alpha$  be  $t^\circ$  warmer than the bottom end, and assume, for our immediate purpose, a uniform gradient of temperature from top to bottom. Assume that the  $P$  surfaces are at a uniform temperature equal to that of the middle height of  $\alpha$ .

If  $\theta$  is the thermal conductivity of copper,  $\alpha$  being 2 cm long and 0.01 sq. cm in area of cross-section, we shall have, as the amount of heat carried downward through  $\alpha$  by its own conduction in one second,

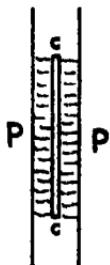


FIG. 9. Figure indicating the packing between the copper plate and the pole caps.

$h = \theta (0.01 + 2) t$ . Meanwhile heat flows out from the upper half of  $\alpha$  through the packing to the surfaces  $P$  and  $P'$ , and the same amount flows back through the packing from  $P$  and  $P'$  to the lower half of  $\alpha$ . If  $\theta'$  is the thermal conductivity of the packing, the amount of heat which it carries per second is  $h' = \theta' (0.2 + 0.25) \frac{t}{4}$ . The ratio of the amounts of heat carried by the packing and the copper, respectively, is  $h' + h = 40 (\theta' + \theta)$ . The value of  $\theta$  may be taken as 0.9 and that of  $\theta'$ , according to Kaye and Laby and my own previous observations (1925 paper), as 0.0002, which makes  $h' - h = 0.01$  approximately.

This may be taken as indicating that the temperature-gradient at mid-height of  $\alpha$  is about one per cent less than it would have to be if it carried all the heat now carried in part by the packing. But we cannot from this conclude that the mean temperature-gradient from top to bottom of  $\alpha$  is reduced to this extent. The gradient must be somewhat steeper at the top and the bottom of  $\alpha$  than at the middle, to take care of the outflow and the inflow through the packing. I

shall assume that the correction called for is an addition of 0.5 per cent to the observed value of  $P$ .

Thus corrections (b) and (f) add 8.5 per cent to the observed  $P$  values, giving, as final values,

TABLE 5

Temperature	$P \times 10^6$
22.5°	-1.441
56.7°	-1.550
91.4°	-1.703

*The Nernst Effect.* In dealing with the Nernst and the Righi-Leduc effects the main difficulty is presented by the longitudinal temperature-gradient, usually about 0.8° C per cm. As I have already shown in discussing Figure 5, this gradient is studied thermo-electrically by means of fine (no. 36) constantan wires soldered to the copper plate at the points 1', 2', 3', 4', 5', with 1 cm intervals. Unfortunately these junctions of copper and constantan are not the only sources of thermo-e.m.f. in the measurement circuits, and the resulting disturbances are not usually equally great in the different circuits, the 1'-2' circuit, the 2'-3' circuit, etc. The observations, made by a null method, with the various circuits will give, approximately, the temperature intervals between points 1' and 2', 2' and 3', etc., but these temperature intervals will not usually indicate a smooth temperature-gradient curve along the copper plate. By making two curves, one for a westward and one for an eastward flow of heat through the copper, and studying these curves carefully I made what I believed to be a reasonably accurate estimate of the average temperature-gradient existing at mid-length of the plates during a double set of observations; that is, one set made with a *W* flow and the other with an *E* flow of heat. I plotted and studied a pair of curves for each of the three mean temperatures of my observations. This was my procedure previous to 1937.

About April 5, 1937, I made an improvement in my apparatus by introducing the device, already described in the discussion of Figures 5 and 7, for equalizing the temperatures of the junctions where the no. 36 constantan wires leading from points 1', 2', etc., on the plate meet the no. 28 constantan wires. I now used also a thermostated oil-bath for the junctions where the no. 28 constantan wires meet the copper wires of the galvanometer circuit.

With these bettered conditions I found on combining *W* and *E* observations that the longitudinal temperature-gradient could be

taken as uniform between points 1' and 5', and in later practice I measured this gradient by observations with the 2'-4' circuit alone.

My Nernst effect measurements lie in two groups, those of 1934 or 1935 and those of 1937. In the meantime all the connections with the copper plate had been broken and renewed. I shall give equal weight to the mean values of the two groups at the given temperatures. I thus get Table 6.

TABLE 6

	$Q \times 10^4$	T
From the measurements of '34 or '35	-2 001	at 24 8°
From the measurements of 1937	-1 990	at 25 0°
Means	-1 995	at 24 9°
From the measurements of '34 or '35	-1 935	at 54 1°
From the measurements of 1937	-1 965	at 54 6°
Means	-1 960	at 54 4°
From the measurements of '34 or '35	1 869	at 84 5°
From the measurements of 1937	-1 866	at 83 7°
Means	-1 868	at 84 1°

The mean values thus found at the various temperatures show a small decrease of  $Q$  with rise of temperature. These values when plotted against temperatures do not lie on a straight line, but I do not attach importance to that fact. Lowering the mid-temperature value of  $Q$  about 1 per cent would make the line straight. I could find a more or less plausible excuse for doing this but prefer not to use it.

The one correction to be applied here is (b), the same as in case of the Hall effect, an increase of 8 per cent. This makes the final values

TABLE 7

Temperature	$Q \times 10^4$
24 9°	-2 155
54 4°	-2 106
84 1°	-2 017

*The Righi-Leduc Effect.* Before giving detailed results of my measurements of this effect I have to mention certain questions to which variations of procedure in these measurements gave the answers.

All my measurements of the four transverse effects except the Righi-Leduc measurements of May 13, 1937, were made at one-

minute intervals, thus giving about 50 or 55 seconds, after application of the magnetic field, for the conditions in the copper plate to become steady. The build-up of the magnetic field to full strength required a perceptible time, perhaps as much as 10 seconds, and it cannot be assumed that the transverse temperature-gradients, the Ettingshausen and the Righi-Leduc effects, reach full value as soon as the field-strength does. In fact, I had some doubt as to whether one-minute intervals were long enough in the case of these two effects. So on May 13, 1937, I made observations of the Righi-Leduc effect at one and a half-minute intervals, thinking I might find a greater value of  $S$  in this way. I found in fact a somewhat smaller value than usual, as figures presently to be given will show, and concluded from this evidence that the one-minute intervals had been satisfactorily long for my purpose.

It is to be noted that, while all of the Righi-Leduc measurements of 1934 or 1935 were made at full atmospheric pressure, the 1937 measurements, except those of May 12, were made with a very much reduced air-pressure about the plate. The fact that so little change in the observed value of  $S$  occurs with change of air-pressure from 76 cm to 0.5 cm of mercury makes it doubtful, as I have already said, whether the use of reduced air-pressure is called for in these measurements. Reduction of air-pressure should reduce the disturbance due to the convection, as distinguished from the conduction, of heat in the neighborhood of the plate. Possibly with a metal of lower thermal conductivity than copper convection might be more important.

Three double-set ( $W$  and  $E$ ) measurements made in 1934 or 1935 under full atmospheric pressure gave the following mean values: temp =  $24.7^\circ$ ,  $S \times 10^7 = -2.491^\circ$ .

Giving the 1937 data in some detail I get Table 8.

TABLE 8

Date	Temp	$S \times 10^7$	Air-press	Intervals
Mar 1	25.0	-2.491	0.4 cm	1 min
May 11	24.9	-2.486	0.5 cm	1 min
May 12	25.0	-2.514	76 cm	1 min
May 13	25.1	-2.454	0.5 cm	1.5 min
Means	25.0°	-2.486		

Combining these means of four measurements with those given above for three measurements, and giving all the individual measurements equal weight, I get

<i>Temp</i>	$S \times 10^7$
24.9°	-2 488

At the mean temperature, near 54°, I made five measurements in 1934 and 1935, all at atmospheric pressure, getting as means 53.9° and -2.266. The one measurement of 1937, with air-pressure 0.4 cm, gave 54.7° and -2.241. Combining these values, giving equal weight to all individual measurements, I get

<i>Temp</i>	$S \times 10^7$
54.0°	-2 262

At the high temperature I made four measurements in 1934 and 1935, all at atmospheric pressure, giving the means 84.4° and -2.091, and one measurement in 1937, at 0.4 cm, getting 83.5° and -2.120. Combining these values, giving equal weight to the individual measurements, I get

<i>Temp</i>	$S \times 10^7$
84.2°	-2 097

The correction to be applied to  $S$  values is the same as that made with the  $P$  values, 8.5 per cent to be added. This gives as final Righi-Leduc effect values

TABLE 9

<i>Temp</i>	$S \times 10^7$
24.9°	-2 699
54.0°	-2 454
84.2°	-2 275

The 54° value of  $S$  would have to be raised rather more than one per cent to make all the  $S$  values lie on a straight line when plotted against temperatures, but I have no good reason for making such a change. Here, as in the case of the Ettingshausen effect and the Nernst effect, the question whether the temperature coefficient is constant is left in doubt by my measurements.

Plotting temperature curves for all the effects except  $R$ , for which such a curve is unnecessary, I get the following table of values for three temperatures

TABLE 10

Temp	$R \times 10^4$	$P \times 10^9$	$Q \times 10^1$	$S \times 10^7$
25°	-5.36	-1.446	-2.155	-2.698
55°	-5.37	1.544	-2.104	-2.448
85°	-5.38	-1.674	-2.014	-2.272

An application of these values in equations given by the author's dual theory of conduction was published in the Proceedings of the National Academy of Sciences for December, 1937, pp. 600-603.



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## RECORDS OF MEETINGS

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One Thousand Two Hundred and Thirty-Second Meeting

OCTOBER 14, 1936—STATED MEETING

The Academy met at its House at 8:20 P. M.

The PRESIDENT in the Chair

There were present sixty-eight Fellows and six guests

The records of the meeting of May 13 were read and approved

The Corresponding Secretary reported the receipt of letters accepting Fellowship from James Waterhouse Angell, Oswald Theodore Avery, Stoughton Bell, Howard Landis Bevis, Wilfred Bolster, James Cummings Bonbright, Harold Simmons Booth, Claude Raymond Branch, Charles Sidney Burwell, Philip Cabot, Robert Pierce Casev, Edward Hastings Chamberlin, Charles Thornton Davis, Fred Rogers Fairchild, Frank Albert Fetter, Albert Baird Hastings, William Clifford Heilman, Frederick Lee Hisaw, Murray Philip Horwood, Ernest Hamlin Huntress, Morris Bryan Lambie, Roswell Cheney McCrea, Malcolm Perrine McNair, Dumas Malone, Elton Mayo, Avery Adrian Morton, Philip Stanley Parker, Henry Parkman, Jr., Stanley Elroy Qua, Thomas Henry Sanders, Donald Scott, Sidney Post Simpson, Clair Elsmere Turner, Joseph Henry Willits, and of letters accepting Foreign Honorary Membership from Edward Victor Appleton, Miguel Asin y Palacios, Marcel Aubert, Raoul Blanchard, Paul Kretschmer, and Jean Hyacinthe Vincent

He also reported the receipt of letters resigning Fellowship from Harry Ellsworth Clifford (Class I, Section 4) and Henry Richardson Shepley (Class IV, Section 4)

The Corresponding Secretary announced that the Council had appointed George Grafton Wilson Vice-President for Class III for the unexpired term of Edwin Francis Gay, who had become a non-resident Fellow and had therefore resigned the Vice-Presidency

He also reported that the second Wednesday of November being a holiday, November 11, Armistice Day, the Council had voted that the November 1936 meeting of the Academy be held on November 18

The Corresponding Secretary announced that the Council had made the following grants from the Permanent Science Fund

1 To Professor James A Beattie, Massachusetts Institute of Technology, Cambridge, \$500, to provide a technical assistant to enable him to make the necessary computations in the evaluation of certain thermodynamic data obtained in an investigation of pressure effects on various thermometric scales

2 To Professor Elery R Becker, Iowa State College, Ames, \$500, for expenses connected with an investigation of the effects of food constituents on coccidians

3 To Professor Robley D Evans, Massachusetts Institute of Technology, Cambridge, \$500, for the purpose of purchasing apparatus to be used in his study of radium poisoning

4 To Professor J Horace Faull, Arnold Arboretum, Jamaica Plain, Mass., \$300, to aid him in making a trip to Guatemala and other southern countries to enable him to collect material on rusts that alternate between coniferous, angiospermous, and filicinean hosts

5 To Dr Millard F Manning, University of the City of Toledo, Toledo, Ohio, \$125, toward the purchase of a computing machine to be used in making theoretical calculations of the electronic energy bands in metals

6 To Professor R K Nabours, Kansas State College of Agriculture, Manhattan, \$350, to help defray his expenses in collecting specimens of grouse locusts (*Tetriginae*) in the regions around Tampico and Vera Cruz, Mexico

7 To Professor Alden E Noble, College of the Pacific, Stockton, Cal., \$312, for technical assistance in the preparation of microscope slides and for work connected with studies on the trematode fauna of the marine fishes of Monterey Bay, Cal

8 To Professor Thomas L Smith, College of the Ozarks, Clarksville, Arkansas, \$100, to be used in continuing his studies of induced mutations in the wax moth, *Galleria mellonella*

9 To Professor William F Windle, Northwestern University Medical School, Chicago Ill., \$500, to aid him in employing a technician in his study of the development of foetal behavior as correlated with intrinsic growth of the nervous system

The President announced the death of six Fellows Charles Thornton Davis (Class III, Section 1), John Hays Hammond (Class I, Section 4), Harry Wheeler Morse (Class I, Section 2), Arthur Amos Noyes (Class I, Section 3), Percy Goldthwait Stiles (Class II, Section 3), Francis Henry Williams (Class II, Section 4), and of three Foreign Honorary Members Henri Louis LeChatelier (Class I, Section 3), Antoine Meillet (Class IV, Section 3), Sir Arnold Theiler (Class II, Section 4).

The Fellows elected in May were then presented to the Academy  
The following communication was presented

Mr Arthur D Nock "The Genius of Mithraism"

The following papers were read by title

"Ecological Relations of Ponerine and other Ants to Termites," by William M Wheeler; "Uncertain Inference," by Ronald A Fisher, "The Respiratory Metabolism of the Chimpanzee," by John M Bruhn and Francis G Benedict, "Insects and Arachnids from Canadian Amber," by F M Carpenter and C T Brues, "Shearing Phenomena at High Pressure, particularly in Inorganic Compounds," by P W Bridgman

The meeting was dissolved at 9 15 P M

One Thousand Two Hundred and Thirty-Third Meeting

NOVEMBER 18, 1936—STATED MEETING

The Academy met at its House at 8 15 P M

The PRESIDENT in the chair

There were present forty-six Fellows, one Foreign Honorary Member, Professor D'Arcy Wentworth Thompson, and four guests

The records of the meeting of October 14 were read and approved

The Corresponding Secretary reported the receipt of letters resigning Fellowship from Truman L Kelley and Francis P Magoun, Jr

He also announced that the Council had reappointed Mr F N Robinson for four years as a delegate from the Academy to the American Council of Learned Societies

The President announced the death of one Fellow, Frank Arthur Laws (Class I, Section 2), and two Foreign Honorary Members Joseph Redlich (Class III, Section 1) and Charles Sanford Terry (Class IV, Section 2).

The following communication was presented

Mr Donald H Menzel and Mr Joseph C Boyce "The Harvard-Massachusetts Institute of Technology Eclipse Expedition to Siberia," illustrated with lantern slides

The meeting was dissolved at 9:25 P M

**One Thousand Two Hundred and Thirty-Fourth Meeting**

**DECEMBER 9, 1936—STATED MEETING**

The Academy met at its House at 8:15 P M

The **PRESIDENT** in the Chair

There were present forty-three Fellows and one guest

The records of the meeting of November 18 were read and approved

The following communication was presented

Dr Fred B Land "The Many-Sided Galen"

The following papers were ready by title "An Experimental Study of the Absolute Temperature Scale," by James A Beattie, in three parts, "Polymorphic Transitions of 35 Substances to 50,000 Kilograms per Square Centimeter," by P W Bridgman

The meeting was dissolved at 9:25 P M

**One Thousand Two Hundred and Thirty-Fifth Meeting**

**JANUARY 13, 1937—STATED MEETING**

The Academy met at its House at 8:25 P M

The **PRESIDENT** in the Chair

There were present twenty-five Fellows

The records of the meeting of December 9 were read and approved

The President announced the death of three Fellows Oliver Lanard Fassing (Class II, Section 1), Francis Greenwood Peabody (Class IV, Section 1), and Julius Oscar Stieglitz (Class I, Section 3)

The following communication was presented

Mr Nathan Isaacs "Political, Legal, and Economic Logic—and Logic"

The meeting was dissolved at 9:20 P M

**One Thousand Two Hundred and Thirty-Sixth Meeting****MARCH 10, 1937—STATED MEETING**

The Academy met at its House at 8 17 P M

The Senior Vice-President, Dr Walter B Cannon, in the Chair

There were present fifty-six Fellows and ten guests

The records of the meeting of January 13 were read and approved

The Corresponding Secretary reported the receipt of letters resigning Fellowship from Frederick S Converse and Alpheus G Woodman

The Presiding Officer announced the death of Ehhu Root, Fellow in Class III, Section 1, and of Sir Frederick Pollock, Bart , Foreign Honorary Member in Class III, Section 1

The following communication was presented

Mr Charles F Brooks "Weather Forecasting," illustrated with lantern slides

The meeting was dissolved at 9 55 P M

**One Thousand Two Hundred and Thirty-Seventh Meeting****MARCH 10, 1937—STATED MEETING.**

The Academy met at its House at 8 35 P M

The Senior Vice-President, Dr Walter B Cannon, in the Chair

There were present twenty Fellows and two guests

The records of the meeting of February 10 were read and approved

The Corresponding Secretary announced the appointment of Dr Fred B Lund and Dr Bert H Hill as delegates to represent the Academy at the Centenary celebrations of the University of Athens in April 1937

The Corresponding Secretary reported the receipt of a letter resigning Fellowship from Joshua Whatmough

The Presiding Officer announced the death of three Fellows Edward Curtis Franklin (Class I, Section 3), Robert Battey Greenough (Class II, Section 4), Paul Elmer More (Class IV, Section 1), and of two Foreign Honorary Members Paul Janet (Class I, Section 4), Vsevolod E Timonoff (Class I, Section 4)

He appointed the Nominating Committee as follows

John C Slater, Class I

John W M Bunker, of Class II

John H. Wilhams, of Class III  
 William C. Greene, of Class IV

On the recommendation of the Council the following appropriations were voted for the ensuing year

From the income of the General Fund, \$7,100, to be used as follows

for General and Meeting expenses	\$ 900
for Library expenses	2,000
for Books, Periodicals, and Binding	1,500
for House expenses	2,000
for Treasurer's expenses	700

From the income of the Publication Funds, \$2,240, to be used for publication

From the income of the Rumford Fund, \$2,250, to be used as follows

for Research	\$1,500
for Books, Periodicals, and Binding	250
for use at the discretion of the Committee	500

From the income of the C. M. Warren Fund, \$898.70, to be used at the discretion of the Committee

The following communication was presented

Mr. Clyde K. M. Kluckhohn "The Individual in Navajo Religion"

The following paper was read by title "Postulates for Assertion, Conjunction, Negation, and Equality," by Edward V. Huntington

The meeting was dissolved at 9:35 P. M.

#### One Thousand Two Hundred and Thirty-Eighth Meeting

APRIL 14, 1937—STATED MEETING

The Academy met at its House at 8:35 P. M.

The Senior Vice-President, Dr. Walter B. Cannon, in the Chair.

There were present thirty-seven Fellows and six guests.

The records of the meeting of March 10 were read and approved.

The Corresponding Secretary reported the receipt of a letter from Eldon R. James, resigning his Fellowship in the Academy.

He also announced two changes in the personnel of the Nominating Committee, Harry M. Goodwin, of Class I, replacing John C. Slater, and Arthur N. Holcombe, of Class III, replacing John H. Wilhams.

The Corresponding Secretary announced that the Council had made the following grants from the Permanent Science Fund

1 To Professor Thomas Harper Goodspeed, University of California, Berkeley, \$500, for technical assistance in cytological, genetic, and morphological examination of certain species of *Nicotiana*, as an aid toward the completion of a cytogenetic monograph on this genus

2 To Professor Rachel E Hoffstadt, University of Washington, Seattle, \$250, to purchase animals and material needed in a study of the viruses connected with Myxomatosis of rabbits, and Herpes simplex

3 To Professor Norton A Kent, Boston University, Boston, \$250, to complete the installation of a 30-foot Littrow spectrograph

4 To Professor Gustav J Martin, College of St Teresa, Winona, Minnesota, \$400, for technical assistance and materials needed in an investigation of the chemistry of silicosis, to be carried out in collaboration with Dr L U Gardner, of the Saranac Lake Laboratory

5 To Professors G H Parker and F L Hisaw, Harvard University, \$300, for the construction of two open sea live-cars (for keeping dogfish) These cars are to be used in their studies of color changes and of reproduction in elasmobranch fishes

6 To Dr Roberts Rugh, Hunter College, New York City, \$125, for the purchase of material to be used in a study of the relations and antagonisms of the pituitary and gonad hormones in Amphibia and Mammals

7 To Mr Curtis W Sabrosky, Michigan State College, East Lansing, \$300, in partial support of a visit to certain European museums as a basis of study preparatory toward writing a taxonomic monograph on the dipterous family Chloropidae

8 To Dr A. W. Sellards, Harvard Medical School, a sum not to exceed \$325, for the purpose of having two colored plates (blocks) made to illustrate a paper on the histopathology of murine leprosy

9 To Dr T E Sterne, Harvard College Observatory, \$300, to aid in building highly sensitive thermocouples, for measuring thermal radiation of stars

The Presiding Officer announced the death of Elihu Thomson, Fellow in Class I, Section 2

The following communication was presented:

Mr Frederick L Hisaw "A Modern View of Internal Secretions and Their Regulation of the Sexual Cycles"

The meeting was dissolved at 9 40 P M

One Thousand Two Hundred and Thirty-Ninth Meeting

MAY 12, 1937—ANNUAL MEETING

The Academy met at its House at 8 20 P M

The Senior Vice-President, Dr Walter B Cannon, in the Chair

There were present fifty-two Fellows and one guest

The records of the meeting of April 14 were read and approved

The Corresponding Secretary reported the receipt of letters resigning Fellowship in the Academy from Warren M Persons and Lawrence C Wroth

He also reported the receipt of an invitation to the Academy to be represented by a delegate at the Giotto celebration at Florence, Italy, April 27, 1937, and announced that Alfredo Casella had acted as delegate and that appropriate cablegrams had been sent

The Presiding Officer announced the death of two Fellows George Croft Cell (Class IV, Section 1) and William Morton Wheeler (Class II, Section 3)

The following report of the Council was presented

REPORT OF THE COUNCIL

Since the last report of the Council there have been reported the deaths of seventeen Fellows—George Croft Cell, Charles Thornton Davis, Oliver Lanard Fassig, Edward Curtis Franklin, Robert Battey Greenough, John Hays Hammond, Frank Arthur Laws, Paul Elmer More, Harry Wheeler Morse, Arthur Amos Noyes, Francis Greenwood Peabody, Elihu Root, Julius Oscar Stieglitz, Percy Goldthwait Stiles, Elihu Thomson, William Morton Wheeler, Francis Henry Williams, and eight Foreign Honorary Members—Paul Janet, Henri Louis Le Chatelier, Antoine Meillet, Sir Frederick Pollock, Joseph Redlich, Charles Sanford Terry, Sir Arnold Theiler, Vsevolod E Timonoff

Thirty-four Fellows and six Foreign Honorary Members were elected by the Council and announced to the Academy in May 1936

The roll now includes 774 Fellows and 118 Foreign Honorary Members (not including those elected in May 1937)

The annual report of the Treasurer, Ingersoll Bowditch, was read, of which the following is an abstract

#### GENERAL FUND

##### *Receipts*

Income on hand April 1, 1936	\$2,394 02
From Investments	\$3,208 70
From Assessments	4,130 00
From Admissions	270 00
	<hr/>
	7,608 70
	\$10,002 72
	<hr/>

##### *Expenditures*

Expenses of Library	\$2,060 00
Treasurer's Expenses	846 19
Books and Binding	1,519 80
General Expenses	823 50
House Expenses	2,083 20
President's Expenses	40 00
	<hr/>
Interest on bonds bought	180 41
Income transferred to Principal	320 00
	<hr/>
	\$ 7,873 10

#### RUMFORD FUND

##### *Receipts*

Income on hand April 1, 1936	\$ 348 07
From Investments	2,642 00
	<hr/>

##### *Expenditures*

Purchase and binding of books	\$ 335 00
Research	2,469 36
Transferred to Publication Account	200 00
	<hr/>
Income transferred to Principal	\$3,004 36
	<hr/>
	155 45
	\$ 3,159 81
	<hr/>

## PUBLICATION ACCOUNT

*Receipts*

Income on hand April 1, 1936	\$1,336.93
From Income—Appleton Fund	\$1,140.00
From Income—Centennial Fund	1,603.11
From Income—Rumford Fund	200.00
From Sale of Publications	455.46
From American Council of Learned Societies a/c Lake Publication Fund	3,250.00
From Lake Fund subscriptions	2,453.68
	9,102.25

*Expenditures*

Publications—	
General Fund	\$3,615.70
Lake Fund	5,439.99
	\$9,055.69
Vault Rent—part	4.40
	\$9,060.09
Interest on Bonds bought	\$ 4.79
Income transferred to Principal	117.80
	122.59
	\$ 9,182.68

## C M WARREN FUND

*Receipts*

Income on hand April 1, 1936	\$ 238.31
From Investments	923.83

*Expenditures*

Research	\$ 751.50
Vault Rent—part	2.20
	\$ 753.70
Income transferred to Principal	46.30
	\$ 800.00

## FRANCIS AMORY FUND

*Receipts*

Income on hand April 1, 1936	\$6,108.01
From Investments	2,853.54

	<i>Expenditures</i>
Publishing Statement	\$ 73 50
Interest on bonds bought	257 02
Vault Rent—part	6 60
	<hr/>
	\$ 337 12

**PERMANENT SCIENCE FUND***Receipts*

Income on hand April, 1936	\$ 900 00
<hr/>	
Received for above fund—	
Income	\$7,806 96
Balance grants returned	93 47
	<hr/>
	7,900 43
	<hr/>
	\$8,800 43

*Expenditures*

Grants from above fund	\$7,807 00
Expenses	27 00
	<hr/>
	\$7,834 00

The following reports were also presented

**REPORT OF THE LIBRARY COMMITTEE**

During the year 123 volumes and 31 unbound numbers of serials have been borrowed by 15 Fellows and 18 libraries, and more have been consulted at the Academy. All books taken out have been returned or satisfactorily accounted for.

The number of volumes on the shelves at the time of the last report was 44,765. During the year 437 volumes were added, chiefly by binding serials, making the number now 45,202. This includes 52 purchased from the General Fund, 23 from the Rumford, and 362 received by gift or exchange.

The following appropriations were placed at the disposal of the Librarian during the past year

Balance from General Fund	\$ 838 78
Balance from Rumford Fund	10 71
Appropriation from General Fund	3,500 00
Appropriation from Rumford Fund	325 00
	<hr/>
	\$4,674.49

The expenses charged to the library account during the financial year ending March 31, 1937, were

Salaries		\$2,000 00
Binding		
General Fund	\$753 35	
Rumford Fund	58 75	812 10
Purchase of Books and Periodicals		
General Fund	\$766 45	
Rumford Fund	276 25	1,042 70
Miscellaneous		60 00
		\$3,914 80

There remained an unexpended balance of \$759 69, as follows

General Fund	\$ 758 98
Rumford Fund	71
	\$ 759 69

In accordance with the usual custom this balance will be carried over to next year

Respectfully submitted,  
HERVEY W SHIMER, *Librarian*

May 12, 1937

#### REPORT OF THE RUMFORD COMMITTEE

The Rumford Committee of the American Academy of Arts and Sciences has held four meetings during the Academy year (April 1, 1936, to March 31, 1937), namely, on May 13, 1936, October 14, 1936, December 14, 1936, and February 16, 1937.

It was voted to recommend the award of the Rumford Medal to Dr W W Coblenz of the Bureau of Standards.

The Committee has made the following grants in aid of research in light and heat

1936	No		Amount
Apr 8	330	To Dr Paul C Cross, Stanford University, toward the purchase of a 21-foot grating to be used in studies of molecular spectra	\$ 300
May 13	331	To Professor George R Harrison, Massachusetts Institute of Technology, to cover cost of obtaining highly purified chemical elements for spectroscopic purposes	400
May 13	332	To Professor Percy W Bridgman, Harvard University, in further support of his investigations of thermal and optical properties of substances at very high pressures	400
Oct 14	333	To Dr Newell Gingrich, University of Missouri, for the purchase of a Phillips Metalix copper target X-ray tube, to be used in researches on X-ray diffraction patterns of liquids	395
Oct	334	To Dr Charles E Teeter, Jr, Cambridge School of Liberal Arts, to cover in part the purchase of apparatus for his investigations on the heat capacity at constant pressures and Joule-Thomson coefficient for various gases	300
Dec 14	335	To Professor Donald C Stockbarger, Massachusetts Institute of Technology, in support of his work on calcium fluoride crystallization	400
Total			\$2,195

Respectfully submitted,  
HARLOW SHAPLEY, Chairman

May 12, 1937

#### REPORT OF THE C M WARREN COMMITTEE

The Committee had at its disposal during the fiscal year 1936-1937, \$1,065 84, of which \$1,050 was appropriated to aid scientific investigations.

Since the last annual report grants have been made as follows

Professor Gordon H Scott, of Washington University, \$200, to be

used to continue his researches on the inorganic salts of mammalian organs, tissues and cells with the use of an electron microscope

*Professor Hermann Schnidt*, Technische Hochschule, Vienna, \$150, to continue his researches in the study of intermediate compounds formed in chemical reaction and a detailed examination of the diazotizing process

*Dr William F Ross*, Rockefeller Institute for Research, \$200, to be used to purchase expensive amino acids for a research involving the synthesis of certain peptides

*Professor George Scatchard*, Massachusetts Institute of Technology, \$200, for apparatus needed to continue his research on the determination with the highest degree of precision of freezing point depression, boiling point elevation and vapor pressure

*Dr Lawrence J Heidt*, Massachusetts Institute of Technology, \$300, to purchase a large Cornu Prism to be used

(1) in the study of the effect of certain gases and vapors upon quantum yields in the decomposition of ozone,

(2) in the study of the intramolecular transfer of energy,

(3) in the investigation of change with wave length and temperature of photochemical decomposition products

Seven applications for grants, totaling \$2,060, will be acted upon at the next meeting of the committee

Reports have been received from Messrs Allen, Bradt, Duncan, Heidt, Huntress, Richtmeyer, Ross, Schmidt, Teeter

The papers listed below, which have not been previously reported, describe the results of investigations aided by the Warren Fund. In each case there is an acknowledgment by the author of the assistance received

A B F Duncan "The Ultraviolet Absorption Spectrum of Ammonia III The Absorption Spectra of the Deuteroammonias A Note on Rydberg Series in Ammonia," *Physical Review*, 50, 700 (1936)

A B F Duncan, "The Far Ultraviolet Absorption Spectrum of  $N_2O$ ," *Journal of Chemical Physics*, 4, 638 (1936)

Nelson K. Richtmeyer and C S Hudson "The Rearrangement of Sugar Acetates by Aluminum Chloride Crystalline Cellobiose and Some of its Derivatives," *J Am Chem Soc*, 58, 2534 (1936).

Frederic C Schmidt, Joseph Sottysiak and Herman D. Kluge

"Heats of Solution and Heats of Reaction on Liquid Ammonia,"  
J Am Chem Soc, 58, 2509 (1936)

Carl L A Schmidt and R Brdicks "On the Formation of Carbamates in Solutions of Glycine and of Alanine Containing Sodium Carbonate," University of California Publications in Physiology, Vol 8, No 9, pp 119-128 (1936)

Hermann Schmid "Thermodynamik der Zwischenreaktionen," Zeitschrift fur Elektrochemie, 42, 579-582 (1936)

Hermann Schmid "Uber den Mechanismus der Diazotierung," Ber 70, 421 (1937)

JAMES F NORRIS, *Chairman*

May 12, 1937

#### REPORT OF THE COMMITTEE OF PUBLICATION

During the year 1936-37 the Committee of Publication has held three meetings, and has carried on the rest of its business by conferences and by correspondence Nine numbers of the Proceedings have been published during this year (Volume 71, numbers 3 to 10, and Volume 72, number 1) There have been no Memoirs Of the first series of *Monumenta Palaeographica Vetera* ("Dated Greek Manuscripts," edited by Professor and Mrs Kirsopp Lake), two more fascicles (V and VI) have appeared The Academy has been generously assisted in the publication of this series by a further grant from the American Council of Learned Societies (a maximum of \$6,000, in support of fascicles VI-X inclusive, to be drawn as needed), contingent on the Academy's contributing toward the series a portion of its annual appropriation for publication During the past fiscal year the Academy thus received from the American Council of Learned Societies not only the sum of \$1,250, previously granted, but \$2,000 from the new grant There are at present about 80 subscribers to this series

The amounts received and expended by the Committee during the fiscal year ending March 31st are shown in the following statements

*General Publication Fund**Receipts*

Balance, April 1, 1936	\$1,047 82
Appropriation, 1936-37	2,367 17
Rumford Fund, grant 1936-37	200 00
Sale of Publications	455 46
	_____
	\$4,070 45

*Expenses*

Transferred to Lake Publication Fund	\$ 600 00
Printing, Proceedings, General Fund	2,647 65
Printing, Proceedings, Rumford Fund	200 00
Other expenses, postage, trucking, etc	172 45
Balance, April 1, 1937	450 35
	_____
	\$4,070 45

*Lake Publication Fund**Receipts*

Balance, April 1, 1936	\$ 148 77
Transferred from General Publication Fund	600 00
Subventions from American Council of Learned Societies	3,250 00
Subscriptions received	1,853 68
	_____
	\$5,852 45

*Expenses*

Plates, Fasc V	\$1,365 32
Text and Binding, Fasc V	625 90
Plates, Fasc VI	1,466 57
Text and Binding, Fasc VI	543 90
Plates, Fasc VII	1,351 24
Other expenses, postage, storage, insurance, etc	87 06
Balance, April 1, 1937	412 46
	_____
	\$5,852 45

The Committee has for several years carried on the publications of the Academy in spite of decreasing appropriations. In the Proceedings it is expected to give members preference over non-members, and to maintain a proper balance with respect to the various fields of research. This year it has been necessary to decline several papers by non-members, and to delay the publication of papers by members for which there were not sufficient funds. The publication of one paper by Professor Percy W. Bridgman (71-9) was assisted by a subsidy from the Rumford Fund, the publication of another paper by Dr. John M. Bruhn and Dr. Francis G. Benedict (71-5) was made possible by a subsidy, not included in the figures given above, from the Carnegie Institution.

In the opinion of the Committee there is a question whether in some fields research is not getting ahead of the ability of the Academy to publish the results of research, keeping a fair balance among the various fields, unless the Academy can find more funds, or unless research funds contribute toward the costs of publication.

The retiring Editor wishes to record his appreciation of the efficient services and the sound policies of his predecessors.

Respectfully submitted,

WILLIAM C. GREFENF, *Chairman*

April 30, 1937

#### REPORT OF THE HOUSE COMMITTEE

The House Committee has had at its disposal funds amounting to \$2,766.92, made up as follows:

Balance from previous year	\$ 521.92
Appropriations for 1936-37	2,000.00
Received for use of rooms	245.00
	—
	\$2,766.92

Of this amount the sum of \$2,185.07 has been spent for the routine expenses, janitor, light, power, heat, telephone, etc., and \$143.13 has been spent for upkeep and equipment, making a total expenditure of \$2,328.20, and leaving an unexpended balance of \$438.72.

Meetings have been held as follows:

The Academy	8
American Chemical Society, Northeastern Section	8
Archaeological Institute of America, Boston Society	2
Friends of China, Inc	3
Geological Society of Boston	1
Japan Society of Boston	3
Mediaeval Academy of America	1
New England Botanical Club	9
Surgical Society	1
Thursday Evening Club	1
 Total	 37

The Council Chamber has been used for the Academy Council and Committee meetings, and also by the Trustees of the Children's Museum, the New England Farm and Garden Association, etc

A detailed list of expenditures follows

Janitor	\$ 981 00
Electricity Power	47 71
Light	182 78
Fuel	647 90
Elevator	100 55
Gas	45 00
Telephone	107 13
Water	33 12
Ash tickets	19 80
Upkeep	52 90
Furnishings and equipment	90 23
Janitor's supplies and sundries	20 08
	\$2,328 20

Respectfully submitted,  
S B WOLBACH, *Chairman*

May 12, 1937

On the recommendation of the Rumford Committee, the Academy Voted, to award the Rumford Premium to Dr William Weber Coblenz for his distinguished work in the zone of science comprising heat and light

On the recommendation of the Treasurer, it was *Voted*, that the annual assessment for the ensuing year be ten dollars.

The annual election resulted in the choice of the following officers and committees:

DUGALD CALEB JACKSON, *President*

JAMES FLACK NORRIS, *Vice-President for Class I*

WALTER BRADFORD CANNON, *Vice-President for Class II*

GEORGE GRAFTON WILSON, *Vice-President for Class III*

ARTHUR STANLEY PEASE, *Vice-President for Class IV*

LEIGH HOADLEY, *Corresponding Secretary*

TENNEY LOMBARD DAVIS, *Recording Secretary*

INGERSOLL BOWDITCH, *Treasurer*

HARVEY WOODBURN SHIMER, *Librarian*

CHARLES HENRY BLAKE, *Editor*

*Councillors for Four Years*

OTTO OLDENBERG, of Class I      RALPH E. FREEMAN, of Class III

ROY G. HOSKINS, of Class II      ERNEST F. LANGLEY, of Class IV

*Councillor for Three Years*

ROBERT HENRY PEIFFER, of Class IV

*Councillor for Two Years*

LIONEL S. MARKS, of Class I

*Finance Committee*

THOMAS BARBOUR      PAUL J. SACHS      ALFRED L. RIPLEY

VANNEVAR BUSH

*Rumford Committee*

HARLOW SHAPLEY

PERCY W. BRIDGMAN      CHARLES L. NORTON      GEORGE W. PIERCE

HARRY M. GOODWIN      NORTON A. KENT      GEORGE R. HARRISON

*C. M. Warren Committee*

JAMES F. NORRIS

GREGORY P. BAXTER      FREDERICK G. KYEES      CHARLES A. KRAUS

WALTER L. JENNINGS      REID HUNT      TENNEY L. DAVIS

*Committee of Publication*CHARLES H. BLAKE, *Chairman*EDWIN C. KEMBLE, of Class I      JOSEPH H. BEALE, of Class III  
FRDERIC T. LEWIS, of Class II      ROBERT P. BLAKE, of Class IV*Committee on the Library*HERVY W. SHIMER, *Chairman*RAYMOND C. ARCHIBALD, of Class I      NATHAN ISAACS, of Class III  
THOMAS BARBOUR, of Class II      HENRY B. WASHBURN, of Class IV*Auditing Committee*

GEORGE R. AGASSIZ      ALFRED FORBES

*House Committee*JEROME C. HUNSAKER, *Chairman*

WILLIAM H. LAWRENCE      ROBERT P. BIGFLOW      WALTER E. CLARK

*Committee on Biographical Notices**For Three Years*DAVIS R. DREWRY, *Chairman*      JAMES F. NORRIS*For Two Years*

JOSEPH H. BEALE      ALFRED C. LANE

*For One Year*

TENNEY L. DAVIS      SAMUEL E. MORISON

*Committee on Meetings*

## THE PRESIDENT

## THE RECORDING SECRETARY

JAMES R. JACK      ABBOTT P. USHER  
HUDSON HOAGLAND      SAMUEL H. CROSS

The Corresponding Secretary announced that the following had been elected members of the Academy

## FELLOWS

## CLASS I

- Section 2* Kenneth Tompkins Bainbridge, Cambridge  
 Ernest Orlando Lawrence, Berkeley, Cal  
 George Walter Stewart, Iowa City, Iowa  
 Jabez Curry Street, Cambridge  
*Section 3* John Tileston Edsall, Cambridge  
 Gustavus John Esselen, Swampscott  
*Section 4* Joseph Henry Keenan, Medford  
 Harald Malcolm Westgaard, Cambridge

## CLASS II

- Section 3* Alfred Sherwood Romer, Cambridge  
*Section 4* Walter Walker Palmer, New York, N. Y.

## CLASS III

- Section 1* Joseph Warren, Brookline  
*Section 3* Clyde Orval Ruggles, Cambridge  
 Harry Rudolph Tosal, Belmont  
*Section 4* Henry Southworth Shaw, Exeter, N. H.

## CLASS IV

- Section 1* Clarence Henry Graham, Providence, R. I.  
 Louis Leon Thurstone, Chicago, Ill.

## FOREIGN HONORARY MEMBER

## CLASS IV

- Section 1* Henri Piéron, Paris

The following communication was presented

Mr Percy W. Bridgman "Physical Phenomena at High Pressure"  
 The meeting was dissolved at 10:05 P. M.



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ROBERT BATTY GREENOUGH	F G BALCH 360
PAUL JANET	D C JACKSON 363
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## LEBARON RUSSELL BRIGGS (1855-1934)

Fellow in Class IV, Section 4 1908

LeBaron Russell Briggs, Fellow of the American Academy of Arts and Sciences, and Boylston Professor of Rhetoric and Oratory, *Emeritus*, in Harvard University, died at Milwaukee on April 24, 1934. He was born in Salem, Massachusetts, December 11, 1855, the son of George Ware Briggs and Lucia Russell Briggs. He graduated at Harvard in 1875, and in 1882 received his Master's degree from Harvard. He was tutor in Greek from 1878 to 1881, instructor in English from 1883 to 1885, Assistant Professor of English from 1885 to 1890, Professor of English from 1890 to 1904, and Boylston Professor from 1904 to 1925, when he retired. He was Dean of Harvard College from 1891 to 1902, Dean of the Faculty of Arts and Sciences from 1902 to 1925, Overseer from 1926 to 1932, President of Radcliffe College from 1903 to 1923. In the second half-year of 1918-1919 he was Exchange Professor with France. He received the honorary degree of LL.D. from Harvard in 1900, from Western Reserve University in 1906, and from Yale University in 1917, and the degree of Litt.D. from Lafayette College in 1907.

This factual array of Briggs's achievement merely indicates the scope of his activities. It gives no hint of the spirit which informed them. For example, the honorary degree from Yale was due not only to Briggs the scholar and writer, but also to Briggs the sportsman, who infused athletic relationships among American universities with a spirit of fairness hitherto unknown. Above his enthusiasm for athletics in themselves, played an honesty, a delight in technique, and a simple friendliness, that also shone over his work in the class room, his administration of the Dean's office, and the ordering of his own life. It may be said of the Dean that thousands of men and women, of widely differing interests, knew him as friend, and not one fails in devotion to his memory.

His career had an uncertain start. President Eliot was still young enough to be overcautious when in 1878 he gave Briggs a tentative appointment. To the end of Briggs's life, his lack of dogmatism, his patient tolerance, lent to his convictions a mildness of expression which was sometimes mistaken for unsureness. No one would make such a mistake for long. Behind the shy smile a shrewd intellect, guided by

principle, appraised men, books, and ideas Books and ideas are final commitments, for them there was only acceptance or rejection But men are malleable, and the Dean suspended judgment To this day thousands are better in English syntax, in demeanor, and in general intelligence, not because they are thinking of what Dean Briggs would say—he was far too self-effacing for that—but because, in some mysterious fashion, he set up for each mind the pattern that should be its own He generally opened his classes with a passage from Thoreau, in which the individual is urged to march to his own rhythm, “however faint, however far away” But it must be an honest rhythm

Doubtless his spiritual strength was renewed by the country life which he loved In his place on Long Pond, near Plymouth, he was most at home Here were his horses, his dogs, Robert Browning the cat, and a long succession of pets, some of which moved back with the family for a Cambridge winter From here he dispensed country products—often making the trip himself—to young friends in Cambridge who had need of them He seemed to have always within him the serenity of that countryside,—its unchangingness,—and the native humor of its people In the spring after the war, when the Dean was Exchange Professor in Paris, he and the present writer stood at twilight on the Pont Alexandre III Paris was doing all it could do to live up to the oft-repeated lavender mists and chestnut blossoms “Beautiful,” he said, “but I miss Plymouth”

His writings are not sufficiently known The essays on college life, in spite of changes in undergraduate customs, remain, fundamentally, as wise and as applicable as when they were written His serious verse, such as the Plymouth Tercentenary Ode, is profoundly felt and well-wrought But his Charades in verse probably gave him more pleasure than his serious writings These were his recreation the joyous offering up of scholarship and pedagogy on the altar of wit No one else could have written them

Happy in his family, his friendships, and his career, he remains the pattern of a great life, upheld amid a chaotic era, yet upheld without benefit of the cloisters He was not withdrawn On the contrary, he delighted to share, with anyone who could share, the fruits of his learning He was the most beloved, the most justly beloved, teacher in our history

ROBERT HILLYER

**WILLIAM HUBERT BURR (1851-1934)**

Fellow in Class I Section 4 (1914)

William Hubert Burr was born at Watertown, Connecticut in July, 1851. After studying with a private tutor, he entered the Rensselaer Polytechnic Institute in October, 1868, and was graduated in 1872 with the degree of Civil Engineer.

Following some miscellaneous engineering experience, he returned to Rensselaer in September, 1875, as acting professor of theoretical and practical mechanics. In December, 1876, he was made professor of these subjects, and in June, 1883, was appointed the William Howard Hart professor of technical and rational mechanics. During this period he published several important papers and books dealing with bridge engineering and mechanics. The best known and most important of these is the monumental book entitled "Elasticity and Resistance of the Materials of Engineering," which was first published in 1883 and ran through several editions.

In 1884 he accepted a position with the Phoenix Bridge Company of Phoenixville, Pennsylvania, a leader in the field of metal bridge construction, and remained with this company until 1891, first as assistant to the Chief Engineer and then as General Manager. During this period he played an active part in the development of the methods of design and construction of iron bridges.

In 1891 he left the Phoenix Company to become Professor of Civil Engineering at Harvard College where he remained until 1893, at which time he was appointed Professor of Civil Engineering at Columbia University, which position he held until retirement in 1916 to become Professor Emeritus of Civil Engineering.

During his long connection with Columbia, he achieved distinction in the consulting field comparable with that he had already won in educational circles. President Cleveland appointed him to a public board to investigate the possibility of a one-span bridge across the Hudson in New York City. By appointment of President McKinley he served on boards dealing with the Isthmian Canal problems, and in 1904 he was appointed by President Roosevelt as a member of the famous International Board of Consulting Engineers which decided the question of whether to build at Panama a sea-level or a lock canal. In 1911 he was appointed by the Governor of New York as a

member of the Board of Engineers to advise on the design of the New York State Barge Canal, and he was a consulting engineer on the Water Supply of New York City from 1903 until his death. He also served as consultant to the Port of New York Authority upon bridges built by this organization, including the George Washington Bridge over the Hudson River.

At the time of his death, he was the oldest member, in years of affiliation, of the American Society of Civil Engineers, which he joined in 1874 and in which he served as a Director from 1894 to 1896. In 1891 the Society awarded him the Thomas Fitch Rowland Prize. He was also a member of the Institution of Civil Engineers of Great Britain, which membership he valued highly. Amongst other honors which came to him during his long life was the award by the Japanese Government of the Order of the Sacred Treasure (2d Degree).

For many years he served as a Trustee of the Cathedral of St. John the Divine in New York City. His clubs included the Century Association and the University Club of New York City, and he was also a member of the Pilgrims and of the Society of the Cincinnati.

He was married in 1876 to Caroline Kent Seelye of New York City who died in 1894, and in 1901 he married Gertrude Gold Shipman, a sister of the late Bishop Shipman. The children of his first marriage were George Lindsley of New York City, Marion Elisabeth (Mrs. James A. Mars), and William Fairfield, and of his second marriage, Anne Louise (Mrs. S. Bayard Colgate).

His death occurred in New York City in December, 1931. A fuller account of Professor Burr's life occurs in Volume 100 of the Transactions of the American Society of Civil Engineers.

CHARLES M. SPOFFORD

### GEORGE CROFT CELL (1875-1937)

Fellow in Class IV, Section I 1933

George Croft Cell was born in St. Thomas, Pennsylvania, February 20, 1875, the son of John W. and Mary Ellen Cell. In 1901 he married Cornelia Ella Clark of Kansas City, Kansas. She and two children, Clark Wesley and Cornelia Ella, survive. Dr. Cell received from Baker University the A.B. degree in 1901 and the honorary degree of LL.D. in 1936. At Boston University he was granted the S.T.B.

degree in 1904 and the Ph D degree in 1908. He studied at Berlin University from 1904 to 1907, doing his major work under Professors Riehl, Paulsen, and Harnack. In 1908 he was elected Professor of Historical Theology in Boston University, a position that he held till his death on April 18, 1937.

Dr Cell was a creative mind. Never content with current thought he was always seeking to revise the opinions of the past. His Doctor's thesis was an attempt to prove that Immanuel Kant's relation to theism was different from that which has been commonly held. In an unpublished work on the Christology of the early church he sought to break new paths in this well trodden field. Later he tried to prove that the current view with reference to the relation of Borden P Bowne to William James was mistaken. His study of this subject led him to accept an invitation to write the section on "Die Philosophie in Nord Amerika" for the fifth volume on Ueberweg's *Grundriss der Geschichte der Philosophie*. Still later he wrote an extended work, entitled *The Rediscovery of John Wesley*, in which he sought to revise the traditional conception of John Wesley's relation to Calvinism. This work has attracted wide attention and is destined to have considerable influence on the future study of Wesleyan theology.

Dr Cell was a vigorous writer and inspiring teacher. Though devoting most of his time to the field of Church History he was deeply interested in current political and social questions and seldom failed to enliven his class room lectures by references to current events. He was an ardent advocate of the temperance cause and an enthusiastic "Progressive" in politics. He wrote extensively and spoke frequently on the problems of the day, and always in an able, original, and convincing manner. He was a striking personality and will long be remembered by those who were privileged to know him and to study under him.

ALBERT C KNUDSON

### GEORGE PERKINS CLINTON (1867-1937)

Class II, Section 2 1914

The annual loss to agriculture from the depredations of plant diseases has been estimated to be anywhere from half a billion to three billion dollars. Whatever may be the true figure, it is a serious

loss. The only protection the public has against it is a home guard, smaller than an army regiment in times of peace, composed of fighters armed with that knowledge of the character and habits of the enemy which comes from a thorough training in the botanical discipline termed plant pathology. One of the staff officers of this guard, a distinguished and esteemed member of the American Academy of Arts and Sciences, was lost to the service with the death of George Perkins Clinton, on August 13, 1937. Actually, he was killed in action, for his death came suddenly, after over-exertion on a hot day, while planning new experiments to try to stop the inroads of certain fungous parasites.

Dr Clinton was botanist at the Connecticut Agricultural Experiment Station in New Haven, Connecticut, for thirty-five years. In addition to his duties there, he was lecturer on forest pathology at Yale University from 1915 to 1926, and was research associate in botany at the same institution from 1926 to 1929.

Clinton came from old American stock, of the pioneer type, which had pushed from the East to the Middle West. He was born in Polo, Illinois, on May 7, 1867. His father was not a farmer, but a newspaper man. Nevertheless, he was so deeply imbued with the importance to the country of agricultural welfare that he made this his own paramount concern, receiving recognition from the College of Agriculture of the University of Illinois for his services. The son followed his father's interests in agriculture, though along a different path. He was drawn very early to the study of plants, starting a herbarium when a young boy, to which he continued to add throughout his life.

Formal botanical training began at the University of Illinois, in 1886, under T. J. Burrill, a great teacher and investigator who is best known for his discovery of bacteria as causal agents in plant disease. Here Clinton received the degree of B.S. in 1890, and the degree of M.S. in 1894.

Upon graduation, he became assistant botanist at the University of Illinois Agricultural Experiment Station and assistant in botany on the teaching staff. There he remained for ten years, leaving only to continue study under Professors Farlow and Thaxter at Harvard. Harvard University conferred the M.S. degree on him in 1901 and the Sc.D. degree in 1902. Immediately thereafter, he became attached

to the staff of the Connecticut Agricultural Experiment Station, where he worked happily and successfully to the end.

Absences from New Haven were of short duration, for the job of trying to reduce agricultural losses from endemic or well established plant diseases and to prevent invasions by new ones throughout the entire State of Connecticut, was by no means an easy one. And the journeys undertaken were, for the most part, professional. In 1904, he was sent to Porto Rico by governmental authorities to study coffee rust, in 1908, he was asked to collaborate with Harvard authorities in investigations designed to control the spread of the brown-tail moth and, in 1909, he was sent on an expedition to Japan, financed by Harvard University to obtain a fungus parasitic on the gypsy moth, in the hope that it might be of service in reducing the ravages of that troublesome insect.

At these and other times, Clinton collected fungi in Canada and on the east coast of the United States, in the Mid-Western states, Europe, Hawaii, Japan, Porto Rico, and Panama, thus building up a cryptogamic herbarium which has become known as one of the best in the country. This collection has now been given to the Connecticut Agricultural Experiment Station, together with a large assemblage of literature on plant pathology.

The value of these collecting trips did not lie wholly in adding definite numbers of named specimens, however, or even in making comparisons with types reposing in other herbaria. Clinton was a keen observer, always on the watch for infestations of new diseases or new locality records for old diseases. Because of this capacity, his journeys were notable as scouting expeditions. More than one State Botanist owes his opportunity to repress the predaciousness of a parasite with a fair degree of ease, to the Clintonian eye which had noted an infection new to the locality.

Clinton's scientific papers numbered about one hundred and twenty-five, and date back to 1893. In addition, his extraordinary activity, his mental and physical drive, is shown by the fact that he was the author of eighteen published reports to the Connecticut Vegetable Growers' Association, of twenty Connecticut Agricultural Experiment Station Bulletins of Immediate Information (frequently with others), and of twenty-four Reports in the Proceedings of the Connecticut Pomological Society. Nor was his literary output the sole measure

of his energy. He was a frequent lecturer before various agricultural societies, and he was influential, because his expositions were clear as well as enthusiastic, and his remedies were practical as well as sound in theory. For years, his participation in the various proceedings occupying the attention of the societies devoted to forestry, pomology, and vegetable growing was such that they owed much of their spirit of energy to him. His work on wildfire of tobacco was perhaps the main incentive for the founding of the tobacco sub-station at Windsor.

It is difficult to evaluate properly Clinton's work in plant pathology. He was public health officer to the plant population of Connecticut, and every disease drew his attention. But he was not content to report perfunctorily the numerous types encountered, and to record the efforts being made to control or to eradicate them. The writer has been told, repeatedly, by co-workers in the field, that they always expected something above and beyond the ordinary, even in the routine reports on the plant diseases of the state, and they were never disappointed. Some new observation on a life history, some suggestion on technique, ideas of one kind or another, were always there. Naturally, these notes did not often contain great discoveries, but they were always helpful, and other pathologists could not afford to disregard them.

Specifically, the contributions for which Clinton will always be remembered are those upon the smuts, the downy mildews, the chestnut bark disease, the rusts—particularly the white pine blister rust, the peach yellows, and other mosaics due to filterable viruses, and certain diseases attributable to bacteria.

Clinton was an authority on smuts. He first published a preliminary paper on North American *Ustilagineae* in the *Journal of Mycology* in 1902. This was followed by a complete monograph of 200 pages, published by the Boston Society of Natural History in 1904. Additional taxonomic material appeared in *Flora* in 1906.

But Clinton was an experimentalist at heart rather than a pure taxonomist. His very complete treatment of the downy mildews cleared up dubious points regarding their taxonomic status, it is true, nevertheless, this was because experimental culture, with improved technique, provided the possibility of describing accurately and figuring carefully the various reproductive stages. The outstanding feature of this work was the discovery of the oospores of the late

blight or downy mildew of potatoes, *Phytophthora infestans* (Mont.) De By

Experimentation continued to play a greater and greater part in Clinton's scientific life, as time went on. Sometimes, it was on matters purely practical, as when, among the first, he tested the efficacy and recommended the use of Bordeaux mixture in the control of potato blight. Sometimes, it was in connection with improved technique, as when, about 1924, he developed methods for testing the susceptibility to white pine blister rust of detached leaves, kept in Petri dishes, thus not only cutting down the time of making proper tests but also preventing the possibility of spreading the disease accidentally. He later applied this method to his studies of life histories of various peridermiums. Again, it concerned botanical theory, as when he contributed to the knowledge of the aecial stages of the heteroecious rusts, or when he threw new light on the relations of nematodes to leaf infections of certain greenhouse plants, or when he made such helpful communications on the behavior of tobacco mosaic.

Dr Clinton was a slender, wiry man,—an eastern Cappy Ricks in appearance, with the incredible capacity for work of that beloved character. He was never too busy, however, to help a comrade, or a colleague, to the best of his ability, and his comments never failed to show a keen insight into the problem under discussion. The writer knew him for over thirty years, and at no time heard him say a word about an acquaintance that could be called cheap, or mean, or disagreeable. He was a friend worth having.

The merit of his contributions to agricultural welfare and to botanical science was recognized early by all those in the same line of work. He was so modest and unassuming, however, with such a distaste for self-advertisement, that prima donna honors were never courted. Nevertheless, it was a source of satisfaction to those who knew him when, in 1930, he was elected to the National Academy of Sciences.

Clinton married Anna J. Lighthbody of Pekin, Illinois, on August 9, 1892. There was one child, Harry Lighthbody Clinton. He was killed in France, fighting with the American troops in the World War. This loss saddened the latter part of his father's life. He never lost his sense of acute grief. Work in increasing amounts was his means of escape.

E M EAST

**CHARLES ALLERTON COOLIDGE (1858-1936)**

Fellow in Class IV Section 4 1918

Charles Allerton Coolidge, Architect, was born in Boston on November 30, 1858. As his associations on both sides of the family were with New England, being a descendant of the John and Mary Coolidge who settled at Watertown, Massachusetts in 1631, it is not surprising to find his major activities in the same environment. He was educated at the Hopkinson School of Boston and graduated from Harvard in 1881. Upon graduation, he followed a special course in Architecture at the Massachusetts Institute of Technology, one of the many distinguished architects who for three generations past have received their professional education under the kindly guidance of Professor Ware or Professor Chandler.

After three years in the offices of Ware and Van Brunt and of H. H. Richardson, the firm of Shepley, Rutan and Coolidge was organized in 1886 to carry on the work left unfinished upon the death of H. H. Richardson. The firm of Coolidge and Shattuck succeeded to the responsibilities of the earlier organization, to be in turn replaced by that of Coolidge, Shepley, Bulfinch and Abbott in 1924, of which Coolidge was the senior member until his death. Inheriting the work of such an internationally known figure as H. H. Richardson, these successive firms made notable contributions to architecture in widely scattered parts of this country, as well as in and around Boston. In all of this work Coolidge took an active personal interest which was apparent in the design of individual buildings, marking them strongly with an expression of his personal taste. Notable among his architectural accomplishments are buildings for Stanford University, California, the Ames Building and Buildings of the Old Colony Trust Company, Boston Safe Deposit and Trust Company, Merchants National Bank, Massachusetts General Hospital, Children's Hospital, Boston Lying-In Hospital, and Harvard Freshman Dormitories, Harkness House Units, and the Harvard Memorial Chapel, in Cambridge, Tower Group and Harper Memorial of the University of Chicago, and the Public Library, Art Institute, Corn Exchange Bank Building and Harris Trust Building in Chicago, and buildings for the Rockefeller Institute for Medical Research in New York and Princeton.

Mr Coolidge served the community in which he lived in many capacities—was Park Commissioner for seven years, Clerk of the Home for Aged Men, an Overseer of Harvard College, President of the Boston Society of Architects, Trustee of the Boston Museum of Fine Arts, to mention only a few. Recognition of his qualities came to him from all directions but he particularly valued his position as President of the Society of the Cincinnati as well as being made a Chevalier of the Legion of Honor of France and receiving the honorary degree of Art D from Harvard in 1906.

The unfailing tact and rare charm that characterized all of his social relations endeared Coolidge to a wide circle of friends. Among his intimates he radiated a happy friendliness that belied his advancing years. But no picture of his human relations, whether professional or social, would be complete that did not pay tribute to the inspiration, the balance, the devotion that he received from his wife, Julia Shepley. Her unobtrusive, constant, and self-less care of his every interest was the power that raised his many qualities to their finest expression.

WILLIAM EMERSON

### ROBERT BATTEY GREENOUGH (1871-1937)

Fellow in Class II, Section 4, 1918

Robert Battey Greenough died suddenly February 16, 1937, in his sixty-sixth year.

He was born at Cambridge, Massachusetts November 9, 1871, the son of James Bradstreet and Mary (Ketchum) Greenough. He prepared for college at Hopkinson's School in Boston, graduating from Harvard in 1892 with the degree of A B *cum laude*. The next fall he entered Harvard Medical School from which he graduated in 1896 *cum laude*.

He married Amelia Mackay Goodwin in Cambridge October 16, 1900. His widow and four daughters survive him.

He began his connection with the Massachusetts General Hospital as a surgical house officer on August 1, 1895 and was devoted to that institution throughout his life, passing through various grades up to consulting surgeon which position he held at the time of his death.

In March 1897 he went abroad, spending most of his time in Vienna where he devoted his energies to the study of pathology. This period

had a great influence on his later professional career. He returned to this country in the latter part of 1897 to become associated with Dr John Collins Warren as his private assistant. His interest in tumors was greatly stimulated by Dr Warren. This was soon after the publication of the International Text-Book of Surgery had established Warren's status as a great scholar in surgery. Dr Warren and Dr Oliver were co-trustees of the Caroline Brewer Croft Fund for Cancer Research and Dr Greenough's first article on "Phummer's Bodies in Carcinoma" appeared in the first report of the Committee published in 1900.

In 1905 Dr Greenough was appointed secretary of the Committee, holding that position until 1909 when the Croft bequest, combined with other funds, was placed in the hands of the Cancer Commission of Harvard University.

When the Colis P Huntington Memorial Hospital was built in 1912, Dr Greenough became surgeon of the institution. From 1915 to 1929 he held the position of director of the Commission and acted as consulting surgeon to the hospital up to the time of his death.

During the war, his research was interrupted by his service with the Harvard Unit at the American Ambulance at Neuilly-sur-Seine where he served as surgeon and executive officer and again when he joined the Medical Corps of the Naval Reserve and was on duty at the United States Naval Hospital in Chelsea as Chief of the Surgical Service. Although each of these gave him an opportunity to demonstrate his ability as a general surgeon and to display his wonderful powers as an organizer, it was not the kind of work he longed for and he was glad to get back to research, especially in the field of cancer, and to his services at the different hospitals.

Dr Greenough held various teaching positions at the Harvard Medical School. In 1901 he was appointed Assistant in Surgery, becoming instructor in surgery in 1905 and assistant professor of surgery in 1910. This last position he held until 1932 when he reached the retiring age at the Massachusetts General Hospital and gave up his active service there.

Teaching at the medical school was a very small part of what he did for the advancement of medicine. He is best known for his contribution in the fight against cancer and to this his energies were devoted all the latter part of his life, a fight for which his thorough

knowledge of general surgery fitted in so well with his grounding in pathology, his various hospital appointments, and his tact and organizing ability. The establishment of consultation cancer clinics was his idea, the one at the Huntington Hospital being the first in this part of the country. One at the Massachusetts General Hospital soon followed and now they have spread all over the state and, under the guidance of the American College of Surgeons, throughout the country. At the time of his death he was President of the American Society for the Control of Cancer. He founded the Committee of the American College of Surgeons for the treatment of malignant diseases. He was its chairman for eleven years and continued as an active member in its cancer campaign. He lent his powerful aid when the State embarked on its hitherto untried State cancer hospital at Pondville and he organized the various State cancer clinics.

Always ready for any amount of work, he gave his time freely and generously in talking before the doctors conducting these clinics, helping choose proper men to run them, and aiding in every way when his advice was asked. He was an inspiring teacher and so generous with faults and mistakes of others in starting new ventures that he made few enemies and hosts of friends, especially among the younger men and his own students and assistants. What the profession at large thought of his ability can be judged not alone by his work but by the honors which they heaped upon him. He was a member of the Massachusetts Medical Society, one of its council for several years, and its president in 1934-1935. He was a member of the American Surgical Association. A Fellow of the American College of Surgeons, he was one of the Board of Governors from 1923 to 1925, a Regent from 1924 to 1937, vice-chairman of the Board of Regents and its Executive Committee from 1935 to 1937, and president of the College from 1934 to 1935. He was a Fellow of the American Academy of Arts and Sciences. This list covers only a part of the marks of recognition which came to him.

Dr Greenough's death is a great loss to the profession. It is indeed seldom that a doctor combines such skill in surgery with such an interest in and knowledge of the scientific work that is being done by other workers, and rarer still, to find a general surgeon who contributes really valuable research in the laboratory. Such a man was Robert Greenough and it will be difficult indeed to find any one man to carry on all of his many works.

FRANKLIN G. BALCH

**PAUL (ANDRÉ-MARIE) JANET (1863-1937)****Foreign Honorary Member in Class I, Section 4, 1934**

Born in Paris, France, January 10, 1863, Paul (André-Marie) Janet sprang from a family of culture. His father was Paul Janet, Professor of Philosophy at the Sorbonne, and the young Janet was brought up along the best French lines which lead to a life of scholarly productivity. At nine years of age, he entered the Lycée Louis-le-Grande in Paris, where his father at one time had been professor of logic. While he was still a student at the Lycée, the Paris International Electrical Exposition of 1881 and its attendant International Congress deeply stirred his enthusiasm. Perhaps this was the stimulus which turned him toward physical science. In any event, he completed his work in the Lycée in 1883, entered l'École Normale Supérieure where he studied under Vioille, and from there he departed as an agrégé des sciences physiques in 1886.

Thereupon, at the age of 23 years, he began his active work in creative science and education in a position under the Faculty of Sciences in Grenoble to which he was recommended by Vioille. In 1893 he was made a Professor in the Faculty at Grenoble. In the meantime, stirred by the industrial traditions of Grenoble and the influences of electric-power experiments made in the neighborhood, he turned his principal thoughts toward developing instruction in applied electricity. Aided by the industries of the area, he succeeded in establishing an Institute of Electrotechnics in Grenoble which Institute possessed (for its day) a well developed industrial laboratory. He was among the pioneers of this work in France and soon became a leader on account of his scientific acumen, his enthusiasm for the combination of theory with practice and of teaching with research, and his delightful personal qualities. He was deeply impressed by the importance of such education as an aid in developing industry. In association with his teaching he wrote a number of books in the field of applied electricity.

In 1894, at the instance of Mascart, he was called to the Sorbonne for work in the Physics Department of the University of Paris, and also to undertake the development of the École supérieure d'Électricité, then being established with the aid of the French government under the patronage of the Société Française des Électriciens and with which

was associated the previously established Laboratoire centrale d'Électricité His qualities as the chief officer led to great success for these enterprises

He received many honors and medals, was called upon to sit in numerous national and international committees within the fields of scientific standards of measurement and other aspects of applied science, and not uncommonly was president of such committees At the time of his death, in addition to being a Foreign Honorary Member of the American Academy of Arts and Sciences, he was a member of the French Academy of Sciences, also of those of Roumania and Brazil, and member of the Academy of Technical Sciences of Warsaw, Honorary Professor at the Sorbonne, Honorary President of the Société Française des Électriciens, Honorary President of the International Electrotechnical Commission, Past-President of the International Electrical Congress of 1932, Past-President of the Société des Ingénieurs Civiles, Past-President of the Société Française de Physique, and honorary member of other societies, recipient of the Médaille Ampère in 1913 and the triennial Médaille Mascart in 1930 He was twice a laureate of the French Academy of Sciences and his writings on applied electricity brought various prizes He had represented the French government in scientific conferences abroad and been decorated by the governments of Poland, Roumania, Sweden, and Turkey He was a Commander of the Légion d'Honneur of France

During the past dozen years he gave much thought to preserving memorials of Ampère and it was through his origination that the boyhood residence of Ampère has been preserved An important room in this building will hereafter bear his name, with the inscription "À la mémoire de Paul Janet, Membre d'Institut, 1863-1937, Membre fondateur de la Société des Amis d'André-Marie Ampère Il sauva cette maison de l'oubli et fut un bienfaiteur pour cette musée "

Despite his numerous activities of national and international import, he lived a happy married life and rejoiced in the affectionate association with his devoted wife (daughter of a professor in the Lycée Louis-le-Grand), distinguished children and group of grandchildren.

At memorial ceremonies held on February 24, 1937, at the École supérieure d'Électricité, de Broglie (representing the French Academy of Sciences) expressed the feelings of Janet's colleagues

"Sa carrière, sa vie de savant original et profond, de professeur incomparable, d'organisateur et d'animateur capable de créer de

toutes pièces l'enseignement technique de l'électricité et de le porter, par son effort ininterrompu, au point où vous le voyez aujourd'hui, tout cela fut consacré par des honneurs qu'il méritait hautement et qu'il ne recherchait pas Mais ce qui fait peut-être le principal mérite de Paul JANET c'est d'avoir allié à la culture générale la plus étendue et la plus profonde, toutes les qualités de méthode, de discernement, de connaissance de la nature des choses et de l'esprit des hommes qui sont nécessaires pour passer de la science pure et abstraite aux applications si prodigieusement variées qui constituent aujourd'hui le domaine de l'électricité industrielle "

DUGALD C JACKSON

### FRANK ARTHUR LAWS (1867-1936)

*Fellow in Class I, Section 2 1897*

Frank Arthur Laws was born in Brockton, Massachusetts, of old New England stock, on May 28, 1867 He died in Brookline on November 12, 1936

His boyhood was spent entirely in Brockton, where he attended the public schools, and he graduated from the Massachusetts Institute of Technology in 1889 in the electrical engineering course and later attended courses at Harvard University From 1889 until his retirement from active teaching as Professor Emeritus in 1932, he served continuously on the staff at the Massachusetts Institute of Technology His chief professional interest was in the field of electrical measurements, but he had a keen grasp of many aspects of electrical engineering. He was responsible for the development of the course in electrical measurements and of the technical electrical measurements laboratory at the Institute He was an excellent teacher and had a real personal interest in his students

Professor Laws was retained for a number of years by the Massachusetts Gas and Electric Commission and also did special work in the field of electrical measurements for the Edison Electric Illuminating Company of Boston, the General Electric Company, and other electric light and power companies in New England He was the author of many technical papers dealing with electrical measurements and his book on that subject was outstanding A complete revision of this book had just been completed at the time of his death.

Professor Laws married Harriet P. Burbank of Salem, Massachusetts, in 1901 and their home was always a place of cheer and friendliness. They were both interested in young people, and many students and younger members of the staff, especially through the later years, remember with pleasure his kindness and the warm welcome they always received at his home.

He was a fellow of the American Academy of Arts and Sciences and of the American Institute of Electrical Engineers, and served on the committees of the latter on standardization and electrical instruments and measurements. He was also a member of the Society for the Promotion of Engineering Education and of the University Club of Boston.

RALPH R. LAWRENCE

### HENRI LECHATELIER (1850-1936)

Foreign Honorary Member in Class I, Section 3, 1919

Henri LeChatelier was born in Paris, October 8, 1850, of distinguished ancestry. His father, Louis LeChatelier (1815-1873) was a widely known engineer, Inspector-General of Mines for France, one of the creators of the French National Railways, and, with Sir William Siemens, builder of the first open-hearth steel furnace. His mother, Elizabeth Durand, was descended from a family of artists and geographers.

LeChatelier was educated exclusively in Paris, first at the Collège Rollin where he received the degree of Bachelor of Letters in 1867 and that of Bachelor of Science in 1868. He then entered the École Polytechnique where his father had been before him, but his work was interrupted by the War of 1870 during which he participated in the defense of Paris. He re-enrolled as a mining engineer in 1872 and received his license to teach physical science in 1874.

For several years thereafter LeChatelier served as geographer in South Algiers, returning to Paris in 1877 to spend there the remainder of his life. He became Professor at the École des Mines in that year, Lecturer at the École Polytechnique in 1882, Professor at the Collège de France in 1883 and Professor of Industrial Chemistry and Metallurgy at the École des Mines in 1887. In 1898 he returned to the Collège de France as Professor of General Chemistry of the Faculty.

of Science of Paris, which title he held until he was made Honorary Professor in 1925.

LeChatelier was a profound and prolific investigator. His early researches were concerned with the application of thermodynamics to chemistry, and they yielded results not only of great theoretical, but also of great practical value. For instance, his principle of mobile equilibrium is recognized as of fundamental importance to our understanding of all physico-chemical equilibria, while his studies of the synthesis of ammonia from its elements, in 1901, laid the foundations upon which Haber and Bosch reared a great chemical industry. His later researches, set forth in some five hundred published articles and books, cover a wide field, although they may perhaps all be classified as physico-chemical. They comprise studies of gaseous equilibria, solutions, the allotropy of the elements, particularly carbon, silicon and the metals, explosives, the utilization of fuels, metallurgy and metallography, particularly as applied to steel, clays, silica and the silicates, cements and mortars, the measurement of high temperatures.

LeChatelier, in his later life, occupied a commanding position in chemical science. He was called upon to serve as a member or chairman of a great many committees and commissions concerned with the application of science to industry and public welfare. In 1907 he was elected to membership in the French Academy of Sciences, succeeding Henri Moissan, in 1927 he was made Grand Officer of the Legion of Honor. He received many similar decorations and many prizes and awards from foreign countries, among which may be particularly mentioned the Grand Prize of the International Exposition at St Louis in 1904 and the Davy Medal of the Royal Society of London in 1916. He was an honorary member of many scientific and learned societies, both in France and abroad.

LeChatelier was a brilliant exponent of the best traditions of French science. His intellect was clear, powerful, and disciplined. His interests were broad, his activity extraordinary, his ideals high and exacting. During his youth modern physical chemistry was beginning its phenomenal development, he became one of its great protagonists.

LeChatelier died of angina pectoris on September 17, 1936, at his country estate, Miribel-les-~~é~~chelles (Isère), France, in his eighty-sixth year.

ARTHUR B. LAMB

## PAUL ELMER MORE (1864-1937)

Fellow in Class IV, Section 1 1931

Paul Elmer More, editor and critic, was born in St. Louis, Missouri, December 12, 1864. His parents, Enoch Anson and Katherine Hay Elmer, were of Colonial stock. The father at one time or another pursued trades as different as bookseller and wholesale grocer. He enlisted in the line in the Civil War, and was mustered out as a Commissary Brigadier General.

The prosperity of the family was intermittent, and Paul met the situation by teaching school for three years on the way to the university. Graduating from Washington University in 1887, he took his master's degree there in 1892, and added to it a Harvard M.A. in 1893. Later honorary degrees were, LL.D. from Glasgow and Litt.D. from Columbia and Dartmouth. His graduate studies at Harvard were in Sanskrit and Pali under Professor Lanman. A brilliant fellow student, Irving Babbitt, was already planning a campaign for a new humanism in which Paul More was to share. For two years, 1894 and 1895, Paul More was an assistant in Sanskrit at Harvard, for the years 1895 to 1897 an associate in Sanskrit and Classical Literature, at Bryn Mawr. Then, apparently well launched on an academic career and affianced to the young woman who became his wife, he withdrew to a cabin near Shelburne, New Hampshire, where he passed two years in meditation and in writing. One may surmise that a shrewd intuition of the incompatibility of teaching with his literary ambitions played some part in this retreat.

He had already given gages to literature. In 1890 appeared from the press of the Putnams a thin volume, "Helena and Occasional Poems." Its value today is not much more than that of proving that the proverbially austere critic had been a very susceptible young man. "The Great Refusal, Being Letters of a Dreamer in Gotham," New York, 1894, was a more serious matter. Ostensibly the editor, Paul More was really the author of this strange collection of love letters to a beautiful woman. Like Dante, Paul More embodied in the beauty and loveliness of a fair woman all his own idealisms. The book is in its own fashion a modern "Vita Nuova," and does not deserve the oblivion that has fallen upon it. "The Great Refusal" has the further interest of showing a soul profoundly disquieted in an agnostic position, and likely to seek ultimate refuge in religion.

Within a year of the publication of "The Great Refusal" Paul More was happily engaged to Miss Henrietta Beck, of St Louis. They were both poor, and the long engagement was at least varied and punctuated by the two hermit years at Shelburne. These were fruitful years. In 1898 appeared his most notable book of verse, "A Century of Indian Epigrams chiefly from the Sanskrit of Bhartrihari." The austere and sententious mood of these aphorisms found a congenial interpreter.

Besides these admirable translations, were written a handful of remarkable critical essays for *The Atlantic Monthly* and other magazines.

In 1900 or a little earlier, at thirty-six, Paul More left the Shelburne cabin with an established reputation as a critic, and even with a little money in the bank. On these assets he married and settled at East Orange, New Jersey, as a free-lance critic. That way lay indigency, for such essays as had been eagerly accepted now came back. A critic to print must have his own organ. So it was a happy choice, though doubtless a forced one, when in 1901, Paul More fell back on the literary editorship of *The Independent*. He built up an already strong review department and adorned it with his own essays.

In 1903 he was called to be literary editor of *The New York Evening Post*. He conducted this new enterprise with characteristic thoroughness and energy and contributed many of his most distinguished essays to the *Post's* Literary Supplement.

In 1903 he published the first volume of "Shelburne Essays." These books were to follow in stately succession until 1921 and the eleventh series, constituting the most substantial body of literary criticism written in the English language in our own times. From his earlier essays he chose for the first volume writers who raised broad moral issues,—Thoreau, Emerson, Hawthorne, Carlyle, Tolstoy. But he also dealt sensitively with such contemporary minor writers as Arthur Symons, Lady Gregory, the Irish poets. In a final essay on "The Religious Ground of Humanitarianism" he expounded those morals of dualism which soon made him a leader in the humanist movement.

The remaining ten volumes of "Shelburne Essays" must be characterized in the most general terms. Most of them were published in *The Evening Post* and *Nation*, as journalistic occasion suggested—

anniversaries, the appearance of new editions or biographies. Preferably he dealt with the most serious authors, but he also treated minor figures with perceptiveness, urbanity, and charm. They seemed to disarm the severe moralist in him. Through all these volumes the uniting thread was his moral philosophy of dualism. The eighth series, 1915, presented "Definitions in Dualism," the ultimate expression of his ultimate position as a secular moralist—a position essentially Platonic. The ninth series, "Aristocracy and Justice," treated political and moral issues in an ultraconservative spirit. For me these are Paul More's least satisfactory essays.

What one felt through the hundred or more "Shelburne Essays" was a critic in the tradition of Matthew Arnold, with English and European literature at his easy command, thoroughly versed in the classics and commanding uniquely among critics writing English an intimate knowledge of the sacred books of India. And this richness of erudition Paul More carried with ease, his scholarship was free from pedantry.

His editorship of *The Nation* ended stormily in 1914 at the stormy beginnings of the World War. He retired to Princeton, where the University for many years enlisted him as a lecturer, chiefly to graduate students, on Greek philosophy. An opportune legacy to his wife made his material situation one of ease, while the spiritual *malaise* which is ever evident in his works was driving him back to Christianity.

The remaining twenty years of his life were devoted to working out his own sort of Christianity. It stood on two legs,—the Platonic Idealism and the Incarnation, as making it personal, living and available. A mere enumeration of titles may sufficiently suggest the development of a familiar theme to which he lent a singular novelty, eloquence and persuasiveness. *Platonism* (1917), *The Religion of Plato* (1921), *Hellenistic Philosophies* (1923), *The Christ of the New Testament* (1924), *Christ the Word* (1927), *The Catholic Faith* (1931). Throughout the familiar analysis of Greek philosophy and ethics, and equally in that of Christian theology and heresy, he made the ways of thinking come alive and assume present importance, for he proved that they were still our ways of facing the issues of life, and pregnant with good will for us. He finally found rest in a faith which embraced a God limited by an ineluctable principle of disorder, the

Incarnation (which he resolutely declined to define), some sort of a resurrection and immortality. An enemy of all dogmatisms, and equally of all mysticisms, he associated himself with the Anglo-Catholic Church. He felt a deep human wisdom in its genius for working compromises. His last considerable literary task was the editing, with F. L. Cross, of an anthology of sixteenth and seventeenth century divinity, "Anglicanism" (1935).

Whoever lacks courage to traverse the theological *Mare Magnum* of the eight volumes devoted to Paul More's religion may find the gist of it in "The Sceptical Approach to Religion," 1934. Incidentally he will read Paul More's greatest book—for me the most eloquent and substantial survey of Christian belief and polity since Bossuet's "Discourse on Universal History."

In this religious development probably the influence of his wife counted for much. An ideal helpmate for a man of letters, tempering the high seriousness of her gifted husband always with her humor, and at times with her mockery, she also was a woman of natural, beautiful, and intuitive piety. She died in 1928. Two daughters, Mary Darrah More (Fine), and Alice More (Dumand), followed the family tradition by marrying scholars.

In 1931 Paul More started a new series of "Shelburne Essays," in smaller compass and format, with "The Demon of the Absolute." In it he attacked all absolutisms standing on a sort of probabilism not unlike that of Butler and Paley, but enriching it greatly from Platonic and Hindu precedents. The next volume was "The Sceptical Approach to Religion," 1934. The third volume of "New Shelburne Essays," "On Being Human," contained articles on humanism, which had become a minor interest with him, on its backer, Irving Babbitt, on Proust, James Joyce, and modernistic French Poetry. But in all "New Shelburne Essays" the interest in literary criticism as such is subordinate to morals.

Such considerations suggest the paradox that a man whose allegiance to literary criticism was perhaps always half-hearted after all made himself a literary critic of the first order. But Paul More could do nothing unthoroughly. His amazing reading, his careful and systematic note taking, his amassing of a kind of literary capital in beautifully filed notes, his scrupulous care in preparation and revision of copy—all this might seem exemplary to that professorial *Deutschum* which he heartily deplored.

In the travail of his great work on theology he neglected too long the early symptoms of the malignant disease which had carried off his wife. A drastic operation in the early summer of 1935 prolonged his life for nearly two years, but on terms of extreme physical debility. His mind rose above this, and as he wasted away in his bed he continued to write and revise his older writings. "An Oxford Diary," a personal confession of faith, was prepared for press during these months and finished only a few days before his death. On March 9, 1937, he passed away in his seventy-third year.

Personally he was equally free from vanity and self-depreciation. His manners were both affable and reserved. Ultimate convictions, perhaps ultimate prejudices also, he maintained inflexibly, but defensively rather than aggressively. In short, one may say that in life and in letters he exemplified all the merits and graces of an enlightened Toryism. In our day such an attitude at least has high scarcity value. It was the uniqueness and integrity of his conservatism that made for Paul More many enemies, and makes his loss irreparable for his friends.

FRANK JEWETT MATHER, JR.

### HARRY WHEELER MORSE (1873-1936)

Fellow in Class I, Section 2, 1911

Harry Wheeler Morse was born at San Diego, California, February 25, 1873, son of Philip and Sarah (McDonald) Morse. He graduated from Leland Stanford Jr. University with the A.B. degree in 1897. He entered the University of Leipzig in 1899 and studied Physical Chemistry with Professor Wilhelm Ostwald and Professor Robert Luther, obtaining a Ph.D. degree in 1901. From 1900 to 1902 he was assistant in Ostwald's laboratory at Leipzig. At that time a large group of American, English, and Russian, as well as German, students of physical chemistry were resident at Leipzig and were eagerly and enthusiastically pursuing their studies and researches in Ostwald's crowded laboratories. Morse, as assistant to Ostwald and Luther, genially and ably aided in the direction of the laboratory *Praktikum* and in the orientation of students in their researches. He also contributed largely to the publication of a revision of Ostwald's *Handbuch*.

and assisted with the work of editing the *Zeitschrift für physikalische Chemie*

In 1902 Morse was called to Harvard as Instructor in Physics for the purpose of embodying in the instruction at the Jefferson Physical Laboratory at Harvard some of the physical material newly arrived at through the vigorous progress that had been made in physical chemistry. In addition to aiding in elementary laboratory instruction, Morse gave lectures at Harvard on photography, electrolytic conduction, and storage batteries, and in his researches made important contributions to these subjects and to the subjects of electrolytic condensers, chemical diffusion, fluorescence, colloidal processes, evaporation, and crystallography. On August 8, 1904, he married Isabel Grace Gray of Ayr, Scotland.

In 1910, after serving eight years as instructor, he was made Assistant Professor of Physics at Harvard. This position he resigned in 1912 to become Professor of Chemistry at the University of California.

Morse was a man of great diversity of scientific interests as shown by his holding successively two important professorships, one in Physics and one in Chemistry. In both of these subjects he was a brilliant lecturer and able investigator.

In 1913 Morse became interested in the inventions of Cottrell for the precipitation of smoke and the recovery of minerals from the flue gases of smelters, resigned his professorship at California, and from 1913 to 1918 he was in charge of the scientific work of the Western Precipitation Company and at the same time was technical manager of the American Trona Corporation. From 1920 to his death he was a consulting chemist and metallurgist, and made many important contributions to metallurgy and mining.

His publications included a translation into English of Ostwald's *Letters to a Painter on the Theory and Practice of Painting*, 1906, and of Ostwald's *Fundamental Principles of Chemistry*, 1907. He was joint author with Ostwald of Ostwald and Morse's *Elementary Modern Chemistry*, 1907, and author of *Chemistry and Physics of the Lead Accumulator*, 1912. He also published a number of monographs on spectroscopy, fluorescence, diffusion, electrochemistry, metallurgy, and geological chemistry.

He was a Fellow of the American Academy of Arts and Sciences,

Member American Institute of Mining and Metallurgical Engineers,  
American Chemical Society, American Institute of Chemical Engineers,  
Sigma Chi, and of the Players' Club of New York

He died at his home at Stanford University, California, March 16, 1936, and is survived by his widow, Isabel Gray Morse, and their four children, Philip Gray, Cecily, Constance, and Anthony John.

He was a scholar of wide interests, a careful and fluent writer, an able and enthusiastic investigator, a genial companion, and staunch friend.

GEORGE W. PIERCE

### EDWARD LEAMINGTON NICHOLS (1854-1937)

Fellow in Class 1, Section 2, 1901

Edward Leamington Nichols was born in Leamington, England, on September 14, 1854, of American parents. After his graduation at Cornell in 1875 he studied at the universities of Leipzig, Berlin, and Göttingen, from the latter university he received the degree of doctor of philosophy in 1879. During the year 1879-80 he held a fellowship in the Johns Hopkins University and in the following year was one of the assistants of Edison in the famous Menlo Park Laboratory. His first teaching position was that of professor of physics and chemistry in Central University, Kentucky, where he remained for two years. In 1883 he went to the University of Kansas as professor of Physics and Astronomy and in 1887 returned to Cornell, where he remained as head of the department of physics until his retirement from teaching in 1919. He died in West Palm Beach, Florida, on November 10, 1937.

Nichols was a firm believer in the value of scientific research to humanity and contributed through his work as an experimental physicist to almost every branch of the physics of his day. His chief interest, however, was in problems connected with light. His activity as an investigator began while he was still a student and extended to within only a few years of his death. Neither lack of facilities nor pressure of other duties could lessen his interest or greatly reduce his activity. During his first two years as a teacher, located in the mountains of Kentucky many miles from a railroad and with no facilities whatever for experimental work, he nevertheless carried on a difficult investigation on the undercooling of vapors and compressed gases. And his experimental work on luminescence continued with-

out interruption even when he was carrying a double load of responsibility as head of the department of physics and at the same time dean of the college of Arts and Sciences

While in Kansas, and for a number of years thereafter, his work was largely in the fields of physiological optics and illumination. Undoubtedly his interest in these lines of work had been greatly stimulated by his contact with Edison during the early development period of the incandescent lamp. His important work in this field led to his election as the second honorary member of the Illuminating Engineering Society, Edison being the first. For the last thirty years he had devoted himself to the experimental study of the luminescence of solids and liquids. His work in this field received support from the Carnegie Institution of Washington, of which he was for many years a research associate. In recognition of his work in these fields, in each of which he was a pioneer, he was awarded the Elliott Cresson Medal of the Franklin Institute, the Ives Medal of the Optical Society, and the Rumford Medal of the American Academy (1928) and was made an honorary member of the Illuminating Engineering Society and of the American Optical Society.

Nichols' work as an investigator represents only one part of his service to American physics. In many other ways his stimulating influence has been important and far reaching.

Aside from his own research work his most outstanding contribution to American physics was the establishment of the Physical Review in 1893. Previous to that time there was no journal in this country devoted exclusively—or even primarily—to physics and the need of more adequate provision for publication had been keenly felt. With the financial support of Cornell University, Nichols established such a journal six years before the American Physical Society was organized and when the number of active physicists in this country was far too small to make any cooperative plan of publication practicable. He remained editor-in-chief of the Physical Review until it had become self-supporting and then transferred control of the Journal to the Physical Society.

To estimate the importance of Nichols' service to American Physics we must recall the conditions in this country at the time he began his scientific career in 1880. There was no general interest in physics, or in science generally, and very little appreciation of the importance of

scientific work. Very few universities were equipped for anything more than undergraduate instruction in the sciences, and in the minds of many there existed a feeling that scientific investigation was hardly a proper function of the college teacher. Not only was there no journal of physics for the publication of results but except for the annual meeting of the American Association for the Advancement of Science there was no opportunity for physicists to get together for discussion. Even when conditions otherwise were favorable it was almost impossible to obtain financial support for scientific work.

Nichols contributed more than any other physicist of his generation to change this situation and to prepare the way for the remarkable scientific progress of recent years. Almost as important as his establishment of the Physical Review was the inspiration of his enthusiasm and untiring scientific activity. He was one of the small group that organized the American Physical Society in 1899 and later one of the society's most active members. As president of the Physical Society, of Sigma Xi, and of the American Association for the Advancement of Science he kept continually before the public the importance of scientific work. His influence was exerted even more effectively through his students. Shortly before the time of his retirement the heads of the departments of physics in thirty-five colleges in this country and in Canada, fifteen of them state universities, were men who had received their physics training from him and with it his firm belief in the value of scientific research and some measure of his enthusiasm.

For one who was as successful as he in a special field Nichols's interests and information extended over a surprisingly wide range. He was by no means a narrow specialist. Undoubtedly this breadth of knowledge and interest was an important factor in making him so successful as a teacher. He was an enthusiastic traveler and, although his sabbatical leave was usually spent in Europe, had visited at some time each of the six continents. A sincere and active church member, Nichols saw no conflict between science and religion, but merely two different aspects of that search for truth to which his life had been devoted. He will be held in affectionate remembrance by all who knew him, but especially by those of us who as his students and associates received encouragement and inspiration from his life work.

ERNEST G. MERRITT

**HENRY FAIRFIELD OSBORN (1857-1935)****Fellow in Class II, Section 3, 1901**

Professor Osborn will be remembered for the unprecedented development of the American Museum of Natural History during his forty-five years association with it and for his researches in and popularization of biology, vertebrate paleontology and evolution.

He was born August 8, 1857 at Fairfield, Connecticut, son of William Henry Osborn and Virginia Reed (Sturges) Osborn. He died suddenly of heart failure at his home in Garrison-on-Hudson, New York, on November 6, 1935 at the age of seventy-eight.

He received an A B degree from Princeton in 1877. As an undergraduate he had become interested in paleontology and so in 1877 with his school friend, W B Scott (now Professor Emeritus of Paleontology at Princeton University) and Francis Speir, Jr. he organized an expedition to explore the Bridger Basin of Wyoming. They brought back to Princeton University many new Eocene mammals.

From 1878 to 1880 he was a graduate student at Princeton University. One year of this time he spent in England where he studied embryology under Balfour and comparative anatomy under Thomas Huxley. He received the Sc D degree from Princeton in 1880 and remained as instructor in comparative anatomy from 1881 to 1890. In 1890 he accepted the DaCosta Professorship of Zoology at Columbia University and at the same time became the Curator of the newly established Department of Vertebrate Paleontology in the American Museum of Natural History. In 1903 he began to transfer to the American Museum the greater part of the lectures and laboratory work of his graduate courses in "Evolution of the Vertebrates" and "Mammals Living and Fossil". He ceased his regular teaching work at Columbia in 1910.

In 1895 he acquired for the American Museum the large private collection of fossil vertebrates which had been amassed by Professor E D Cope of Philadelphia. This contained many of Cope's types. Then under the vigorous and efficient direction of Professor Osborn, the Department of Vertebrate Paleontology began the great series of field explorations for fossil vertebrates which has never ceased to this day.

Upon the death of Mr Jessup in 1908 he was elected President of

the Board of Trustees of the American Museum. This necessitated a curtailment of some of his other activities and he turned over his teaching to his assistant, Professor William K. Gregory, who still continues it most successfully. During this period of his able leadership many buildings were added to the Museum in response to the ever growing pressure of the collections and exhibits. Doctor Osborn became Honorary President in 1933.

During his presidency the endowment of the Museum increased from two million dollars to over fourteen million. The Museum membership increased over 400 per cent. The scientific staff was more than trebled. The earth was dotted with expeditions sent out by the Museum and priceless collections were brought back. Very numerous publications, scientific and popular, were issued and given world wide distribution. The artistic standard and effectiveness of the Museum exhibits were vastly improved in their power to attract attention and convey information. Doctor Osborn regarded the Museum as an educational force of supreme importance in acquainting mankind with the nature of his environment.

Personally, he was optimistic, sincere, and extremely helpful, especially to young students. He had a fertile mind, a broad vision, and tenacious purpose. He constantly respected the rights of his colleagues and students to differ with him in the interpretation of scientific problems. The writer well remembers when, as his teacher, Doctor Osborn deeply apologized to him for adding a summarizing sentence to an article without being able to consult him before it went to the press.

In his teaching and writing he repeatedly emphasized the importance of combining breadth of knowledge and interest with intensive specialization, if science were to avoid a narrow, unimaginative submergence in the mere accumulation of fact and on the other hand were to escape a shallow and superficial veneer of pseudoknowledge. He insisted on the supreme importance of the creative element in science and education.

Evolution was to him a continuous creation of life fitted to a continuously changing world. He frequently summed up the meaning of evolution in the following statement "The moral principle inherent in evolution is that nothing can be gained in this world without an effort, the ethical principle inherent in evolution is that only the best

has the right to survive, the spiritual principle in evolution is the evidence of beauty of order and of design in the daily myriad of miracles to which we owe our existence "

At Princeton in 1876 young Osborn came under the influence of President McCosh who unlike many of his generation taught that the views of Darwin were not incompatible with Christian theology and that evolution seemed to be the method which God had followed in creating the world. He thus started his scientific career with no sense of an irreconcilable conflict with his outlook as a scientist and his faith as a Christian. He was a life long communicant and church-goer.

Doctor Osborn was the author of 940 articles, books and monographs. Among his more important contributions were his monographs on the Mesozoic mammals, the fossil rhinoceroses, the titanotheres, and proboscideans. His books include "From the Greeks to Darwin," "The Age of Mammals," "Origin and Evolution of Life" and "Men of the Old Stone Age." He made many contributions to the study of the evolution of the mammalian molar teeth from their bond with tritubercular type, and also to adaptive radiation, especially in mammals.

Doctor Osborn's contributions to science were recognized here and abroad. He was an honorary fellow of a long series of distinguished societies in Europe, Asia, and America. He was an active member of the National Academy of Sciences. In 1928 he was President of the American Association for the Advancement of Science. Among the many awards received in recognition of his scientific labors were the Darwin medal of the Royal Society of London, the Wollaston medal of the Geological Society of London, the medal of the Pasteur Institute of Paris, and the Prix Albert Gaudry of the Geological Society of France.

HERVEY W SHIMER

### MICHAEL IDVORSKY PUPIN (1858-1935)

Fellow in Class I, Section 2, 1905

Michael Pupin lived a life of fruitful activity for seventy-seven years. He earned distinction in mathematical physics and electrical communications. He had a strong taste for invention in the field of

applied electricity because of its service to humanity, and here he likewise earned distinction. Moreover, he was a philosopher and a romantic. Indeed, he was, himself, a romance.

He was born of peasant parents on October 4, 1858, at Idvor, a village of peasants in the Banat province of old Austria, which was peopled by Serbs, and his parents were of the Serbian race like their neighbors. These people of the Banat were mostly illiterate (in the sense of being unable to read and write) but were full of biblical interpretations, folk-tales, Serbian ballads, and warrior's stories. Young Pupin spent his early years in this peasant setting. His youthful mind was also filled with speculative activity aroused by the stimulating view of wide agricultural lands by day and brilliant stars by night, which views seem to have exerted a deep influence on his mind even while he performed the conventional physical labors of the life of a peasant boy in the pastures and vineyards of the Banat. He never lost from his life the sense of a deep, spiritual philosophy which was implanted in those days. Also, at the instance of an uncommonly sympathetic and wise mother, though herself without formal schooling, he secured the schooling available near home and then attended school at Prague until he was sixteen years of age.

The repressive and narrow outlook in his home land for an ambitious and romantic boy of mental and physical vigor turned his mind and then his being toward America, the land of Benjamin Franklin and Abraham Lincoln. He started for the United States in March, 1874, on his lone responsibility, and he arrived on Manhattan Island, according to his autobiography, possessing only a Turkish fez, the clothing which he was wearing, and five cents in money. He had made the cold and stormy ocean crossing in March without even possessing mattress or bedding for his steerage bunk. He had no relatives nor acquaintances in America and he confessed to the immigration authorities that his knowledge of our nation consisted of little more than the names and some traditions of Franklin, Lincoln, and Harriet Beecher Stowe.

Fortunately admitted to the United States under the then existing liberal immigration laws, he sought for work. The country was still in the clutch of the great depression of the seventies, and work was not plentiful; but, through farm work in Delaware, Maryland, and New Jersey, and odd jobs in New York City and Brooklyn, he made

his way through hardships which only one of great physical endurance and mental purposefulness could have sustained Happily, he fell in with people in lowly walks of life who advised him well His reading was of the great American patriots, and his contacts widened until he was given all-round encouragement to prepare for college. In 1879, the fifth year after arriving in this country, he passed entrance examinations for Columbia University with a high record which admitted him to the University free of tuition fees In college he became equally noted among his classmates for scholarship in mathematics and Greek, and for prowess in wrestling and boxing He was "class president" in his junior year Thereafter his personal qualities, physical vigor, grasp in learning, sound enthusiasm for mental and physical activity of helpful character, and readiness in friendships with interesting people carried him forward throughout his always interesting and ultimately distinguished career He had a genius for friendship with people of intellectual quality and guiding spiritual influence To his great joy he became a naturalized American citizen the day before his graduation into the Bachelor of Arts degree at Columbia in June, 1883

Pupin now possessed a fair acquaintance with the classics and mathematics, but his ambition had become set on science, and particularly on electromagnetism as developed by the works of Faraday and Maxwell His scholarship at Columbia rated him support for further study, and he sailed for Europe to visit his old mother at Idvor for the first time since his departure for school at Prague, and then to enter Cambridge University (England) to study under the spirits of Newton and Maxwell Maxwell had been dead for some four years, and neither Lord Rayleigh nor J J Thomson (who succeeded to physics in the University) were Maxwell devotees This was a disappointment to Pupin, but he remained at Cambridge until 1885, concentrating his study on mathematics, although apparently reading much regarding Faraday, Maxwell, and La Grange In one summer he learned French because "The names of Laplace, La Grange, and Ampère were mentioned so often and with so much veneration by Maxwell that I felt ashamed of my ignorance of the language of France," and then, feeling "enriched by a good knowledge of a great civilization," he read La Grange's *Méchanique Analytique* in the original

Attracted by the reputation of Helmholtz in experimental physics, he migrated to the University of Berlin to study under that master. He was the first holder of a Tyndall Fellowship of Columbia University. It was here that he absorbed with his usual concentration, Helmholtz's notable interpretations of the Maxwellian theories. While thus a student still in Berlin, he heard in the latter part of 1887 an announcement by Helmholtz of Hertz's experimental verification of Maxwell's theory of electrical waves in space, and a eulogy of Hertz who had been a student of Helmholtz. Early in 1889 he received from the University of Berlin the Ph D degree for his work with Helmholtz, which was crowned by a mathematical research and thesis in physical chemistry—a field in which Helmholtz took great interest at the time.

It was in 1888 that Pupin became engaged to Sarah Katharine Jackson, sister of one of his Columbia classmates then also studying in Europe. A beautiful example of his purposeful tenacity lies in his following the girl from place to place in Europe, as she moved about with her mother for visiting and sight-seeing, until she accepted his suit, whereupon he hastened to New York to try to secure a job. Happily that was to be had promptly as "Teacher of Mathematical Physics in the Department of Electrical Engineering" of Columbia University. Thereupon, returning to Europe, he was married in London and returned to Berlin to finish the work for his doctorate.

The autumn of 1889 found him established in his post at Columbia University. Then began his notable creative career in teaching, writing, and inventing. His was an extraordinary influence on students in classroom and laboratory. His five articles published in Transactions of the American Institute of Electrical Engineers in the decade 1890-1900 are now historical classics, as likewise are several articles in other fields published in other journals. Of his three books, published for general consumption, his autobiography called "From Immigrant to Inventor" is a contribution to the literature of American life and idealism.

At the time that he assumed his position in the staff of Columbia University the electrical engineering laboratory was meagre in space and meagre in equipment. The physics equipment of the University was not planned for experimental research. However, Pupin started industriously to work with lean and extemporized equipment toward

the answer to various questions fermenting in his mind. This led to inventions relating to oscillating circuits and rectifier devices, at least some of which later proved of value to the Marconi Company when developing its processes of radio communications.

Upon publication of Roentgen's discovery of X-rays, Pupin started to work actively in research relating to their application in surgery, and particularly to methods of X-ray photography. He also independently discovered secondary radiation of X-rays.

His principal invention, however, made in the latter part of the decade of the nineties, was in loading telephone lines with self-inductance in a manner to improve speech transmission. Thus arose the well-known Pupin "loading coils."

It was already known that addition of self-inductance in overhead telephone circuits would be helpful. Increasing the distance between outgoing and incoming conductors of a pair composing a telephone circuit had been proposed, but was not physically or economically feasible. Introduction of coils at intervals apparently had been tried but proved without utility. Pupin solved the problem by an intellectual process which is a monument to his mental fertility. He was familiar with the well-known La Grange solution of the equation for a vibrating string loaded with pellets. Having achieved a solution which included the effects of abstracting energy by the drag of a viscous medium, he was impressed by the analogy to conditions of flow of alternating current in an electric circuit where it is desired in the process of transmission to preserve the fidelity of an impressed vibratory wave train. He soon had formulas which displayed specifications for the self-inductance to be provided in coils, and the frequency of the location of the coils, in any telephone circuit of known physical construction and desired performance. Experimental tests of models completely verified his theoretical predetermination. The intellectual process of Pupin,—of conception, use of abstract science for drawing inferences together, and verification by laboratory experiment,—place this invention on the high level occupied by the group of the most beautifully intellectual of American inventions.

At the opening of the twentieth century it was thought that this invention was possibly the reed upon which could lean the economical development of telephony through aerial wires over very long distances. It did aid in that direction. On the advent of the triode

vacuum tube and vacuum tube telephone repeaters, they usurped that field, but the Pupin loading coil still holds an important place in many aspects of telephone plant.

At the time of retiring from his active position in Columbia University to become Emeritus Professor, with the intention of continuing in active research, his title was Professor of Electromechanics. This was in 1929. His health was not good in the latter years of his life. He died on March 12, 1935.

He was active in organized affairs relating to science, throughout his life. He became a member of the American Institute of Electrical Engineers in 1890, was its President in 1925-26, and was an Honorary Member at his death. He was a charter member of the American Physical Society, which was organized in 1899, and was a member of the American Mathematical Society. He was President of the Institute of Radio Engineers in 1916 and President of the American Association for the Advancement of Science in 1926. He was Chairman of the Engineering Foundation for a period after the United States entered the World War, was instrumental in the aid which that Foundation gave to the establishment of the National Research Council, and for a time he participated actively in the work of the latter. He was a member of the National Academy of Sciences and the American Philosophical Society, besides other scientific societies at home and abroad. He became a Fellow of the American Academy of Arts and Sciences in 1905.

He is reputed to have received as many as eighteen honorary degrees from educational institutions. His inventions and their service to mankind brought him many medals. In 1902 he received the Elliot Cresson Medal of the Franklin Institute, in 1916 the Prix Hébert of the French Academy of Sciences, in 1920 the Edison Medal of the American Institute of Electrical Engineers and the Gold Medal of the National Institute of Social Sciences, in 1924 the Medal of Honor of the Institute of Radio Engineers, in 1928 the Washington Award of the Western Society of Engineers and the Four Founder Engineering Societies, in 1932 the John Fritz Medal of the Founder Engineering Societies.

Beginning with 1909, he gave much attention to the welfare of Serbian immigrants in this country, and he gave aid to Serbia during the World War.

Those who knew Pupin personally will understand how characteristic of his enthusiasm is the remark made in his autobiography relating to his student days in Berlin while he was ruminating on the works of Faraday and Maxwell and their interpretations by Helmholtz "I do not know how difficult it is to conceal a deep secret, because I never had one to conceal, but I do know how hard it is to keep imprisoned in one's heart the joy which one feels when the light of new knowledge rises above one's mental horizon" The first nine chapters of that autobiography, which bring him to his ultimate academic career, are a contribution to distinguished literature They can be reread with the same lively interest as may be found in rereading the autobiography of Benjamin Franklin or of John Brashear

DUGALD C JACKSON

### ALLAN WINTER ROWE (1879-1934)

Fellow in Class I Section 3, 1927

The many scientific and social activities of Allan Winter Rowe have been recorded in detail in a number of published articles<sup>1</sup>

This memoir will be limited to a brief account of his life and an appreciation of his scientific work Dr Rowe was a cultured gentleman who had many interests outside of his professional life He was an authority on heraldry and a member of the committee granting heraldic designs in New England He was an expert on early pewter, medical history of crime, and New England antiques, and was active in the affairs of the Harvard Musical Association His influence on the development of amateur athletics is recorded in the references which have been given He served his Alma Mater as a member of its corporation and as president of the Alumni Association of the Massachusetts Institute of Technology

<sup>1</sup> Allan Winter Rowe—1879-1934—Some Tributes and a Reproduction of the Portrait Presented to M I T by His Friends, The Alumni Association, M.I.T., July, 1935

Endocrinology, January—February, 1935, page 19

Industrial and Engineering Chemistry (News Edition), December 20, 1934, page 454.

The Nucleus, of the Northeastern Section of the American Chemical Society, February 1935, page 101

The Technology Review, January, 1935, page 140

Bostonia, January, 1935

Allan Winter Rowe was born in Gloucester, Massachusetts on July 31, 1879, and died in Boston on December 6, 1934. He was awarded the degree of Bachelor of Science in Chemical Engineering by the Massachusetts Institute of Technology in 1901. After a year in industry he was appointed an assistant in chemistry at Wesleyan University where he carried out research with Professor W. O. Atwater and won the degree of Master of Science in 1904. He was granted a fellowship by the Massachusetts Institute of Technology and after two years at the University of Göttingen was awarded the degree of Doctor of Philosophy in physical chemistry. He was appointed special lecturer in the Boston University School of Medicine, and in 1908 was promoted to a professorship. During the period between 1908 to 1914, he found time to continue his research in physical chemistry at Harvard University, in collaboration with Professor T. W. Richards. In 1910 when the Evans Memorial Hospital of Boston University was organized for clinical research and preventive medicine, Dr. Rowe became a member of its research staff. In 1921 he was chosen as Director of Research and continued in that position until his death. Dr. Rowe did not have the degree of Doctor of Medicine, his appointment to such an important position was unusual and evidence of the recognition of the value of his work in the field of medicine. The experience gained by Dr. Rowe in his researches in physical chemistry gave him a point of view which is seen in all his work in physiological chemistry. His analysis of the factors involved in his experiments, recognition of causes for errors, quantitative point of view, and his ability to interpret data in a scientific manner led to definite conclusions in a very difficult field of research.

Dr. Rowe's most significant work was in endocrinology. Just before his death he announced that sterility was cured in a significant proportion of human beings by giving to one or the other parent an endocrine gland preparation to make up for hormone deficit. For twenty-five years he devoted himself to the study of the functions of endocrine glands. Much experimental work was devoted to establishing the behavior of the glands in normal health and to developing dependable qualitative and quantitative tests to be used in the diagnosis of disturbed endocrine functions. Dr. Rowe was a pioneer in this field and became a recognized authority. He was a member or

fellow of more than a score of scientific academies or societies in this country and in Europe

Dr Rowe was a forceful and attractive speaker. He had a personality that charmed all with whom he came in contact. He was interested in and helped many people, and had many loyal friends.

JAMES F NORRIS

### JULIUS OSCAR STIEGLITZ (1867-1937)

Fellow in Class I, Section 4 1914

Julius Oscar Stieglitz, an eminent investigator, teacher, administrator, and an important figure in American chemistry, was born in Hoboken, New Jersey, May 26, 1867, a son of Edward and Hedwig Werner Stieglitz. His father who emigrated to the United States during the middle of the last century served in the Civil War and later became a successful wholesale importer of woolens. Julius was the twin brother of Leopold Stieglitz, a physician, through whose influence he might have acquired his life long love of medical science, and the brother of Alfred Stieglitz, the distinguished artist-photographer, art patron, and editor.

At an early age of 14 Julius was sent with his brother Alfred to Germany to study at the Realgymnasium, Karlsruhe, Baden, where he remained until 1886. It was here that he met and courted Anna Maria Steffel who became his wife in 1891. After he finished his secondary education at the Realgymnasium, he spent a year studying chemistry at Gottingen and two years at the University of Berlin where he obtained his Ph.D. degree under A. W. Hoffmann. In 1890, when Clark University had attracted J. U. Nef, Arthur Michael, and other leaders in organic chemistry, Stieglitz came back to America and joined Nef at Clark as a postdoctorate scholar. For a short time after this, he worked with Parke, Davis & Co. and when the new University of Chicago was opened in 1892 and Nef was asked to head the chemistry department, Stieglitz was given the position of a docent.

Early in his career at the University of Chicago, Stieglitz must have shown outstanding qualities as a teacher, research worker, and administrator, since we find him rapidly advancing in rank and importance during the first decade of his service. At this time the research spirit at Chicago was very high. Under the leadership and

enthusiastic support of Nef, outstanding contributions to fundamental chemistry were made by Stieglitz, Alexander Smith, Felix Lengfeld, Herbert McCoy, Lauder W Jones, and their students. It was during this period that Stieglitz made valuable contributions to molecular rearrangements, stereoisomerism of nitrogen compounds, theory of indicators and of color production, positive and negative halogens, and catalysis in organic chemistry. He was a leader in the application of physical chemistry to organic and many of his ideas were frequently backed by precise measurements. With W A Noyes he was the pioneer in the development and application of electronic theories to organic chemistry long before the theories of Lewis, Langmuir, and Kossel were announced. All of this early work brought him considerable recognition a promotion to a full professorship in 1905, a directorship of the analytical laboratories, an invitation to deliver the Hitchcock lectures at the University of California in 1909, and an honorary degree of D Sc from Clark University in the same year.

In spite of all these honors Stieglitz's interest in research was unabated. His fondness for medicine in its relation to chemistry was cultivated through his friendship with Dr John Harper Long and with various members of the medical and biological departments of the University. Early in his career we find him associated with the Council on Pharmacy and Chemistry of the American Medical Association and with the Institute of Medicine of Chicago of which he was President in 1917. He was a member of the Advisory Council of the Otho S A Sprague Memorial Institute for over twenty-five years, and a consultant to U S Public Health Service for over eighteen years. Some of his later work was on organic substances of medicinal value. These include organic compounds of mercury and arsenic and various hypnotics. However, his greatest service to medicine in its relation to chemistry was done through his addresses and books. In 1924 he was the Dohme lecturer at Johns Hopkins University and, in 1925, his "Chemistry and Recent Progress in Medicine" was published followed, in 1928, by a book which he edited on "Chemistry in Medicine". He thought and preached that "chemistry has found in medicine one of its greatest sources of inspiration".

It is not very often that we find an individual who excels equally as an investigator and as a teacher. Stieglitz excelled in both. His

lectures, which were delivered without notes, were clear, unemotional, dignified, logically organized, and leisurely delivered, and were always supplemented with demonstrations of a few well conceived but never spectacular experiments. He had an intuition for what was significant and what was insignificant, a mark of a great teacher. Although his chosen field was organic chemistry, he developed an excellent course in analytical chemistry and in 1911 he published "The Elements of Qualitative Analysis" in two volumes, a textbook which treated this field for the first time from the point of view of physical chemistry and was destined to become a classic in this branch of chemistry. Being a lucid and convincing expositor, he was one of the faculty leaders chosen to organize an "Orientation Course" for the first year students to help them decide what field to pursue. From this course evolved the "Nature of the World and of Man" published in 1926 to which he contributed Chapter V.

Julius Stieglitz was also a shrewd administrator. In 1912, he was made director of the University Laboratories, and in 1915 succeeded Nef as the chairman of the Department of Chemistry. It was in this capacity that he did his greatest service to American higher education. As a member of the University senate he helped mould its policies, he was a strong advocate of postgraduate education of both sexes and at one time had three women in his own staff. Having been trained in Germany during the most impressionable period of his life, he was in the position to evaluate the higher degrees granted by the American Universities. It was his opinion that just before the World War our Ph.D. degree was equal to that granted by the German universities while after the War it was superior, and after that period never advised students to go abroad for their doctor's degree.

His loyalty to chemistry, and particularly to American chemistry, was great. In 1917, during the most critical period of our country, he was elected president of the American Chemical Society, and in his presidential address delivered in Boston he argued in favor of our chemical independence in dyestuffs, medicinal, and other important chemical products. He appealed to the American people at large to recognize the chemical profession at par with the legal, medical, engineering, and other great professions. However, he greatly feared that the development of our great chemical industries would result in the exodus from our universities of their best investigators. He

felt "that healthy progress in our science is dependent primarily on university men pursuing great lines of original investigation To take from our universities the choicest of our research men would deprive our young men of that inspiration and fertilization of their minds in the period of their greatest acceptiveness, which early intimate association with great investigators alone can give To my mind it is clear that if universities would fulfill their highest missions they must remain the seats of the best type of research "

In addition to his early honors, Stieglitz received an honorary degree of Chem D from the University of Pittsburgh in 1916, and the Willard Gibbs Medal in 1923 He was a member of the National Academy of Sciences, a Fellow of this Academy, the Washington Academy of Sciences, the American Philosophical Society, Sigma Xi (president 1917-19), American Association for the Advancement of Science (vice-president, Chemistry Section, 1917), member of the American Chemical Society, and of a number of foreign societies, member of the International Commission of Annual Tables of Constants (1914-20), and a trustee of International Critical Tables (1920-33)

Like many of the great chemists of the past, Stieglitz was an indefatigable worker throughout his whole life, and very seldom was known to take long vacations Due to his shyness and personal sensitiveness, his social contacts, outside of his immediate household, were few although he had many friends He learned to relax in music, photography and, towards the latter part of his life, in golf To his colleagues he was loyal, tolerant, cooperative, and kind To those who sought his wise counsel he was unselfishly generous with his time

In 1932 he lost his wife Anna and in the following year he retired from departmental duties in order to devote the remaining years of his life to research and to writing for publication the numerous researches which were done under his direction during the latter part of his life In 1934 he married Mary Meda Rising, a member of his own faculty for many years Two years later he suffered a heart attack and after five weeks of illness died of pneumonia on the 10th day of January, 1937 He had two children by his first wife, a daughter, Dr Hedwig Kuhn, and a son, Dr Edward Julius Stieglitz.

To perpetuate his memory and his high ideals, a number of friends,

former students, and members of the Chicago Section of the American Chemical Society have recently founded the Julius Stieglitz Lecture-  
ship

NICHOLAS A. MILAS

### ELIHU THOMSON (1853-1937)

Fellow in Class I, Section 2, 1888

Elihu Thomson was born in Manchester, England, on March 29, 1853, and came to this country as a child when his father's employment brought the family to America to locate in Philadelphia. He was the second in a family of eleven children. He evinced great interest in science from early years. When he was eleven years old, his mother provided him with a book called "The Boy's Own Book" that described scientific phenomena together with illustrations of simple apparatus and experiments. The contents of that book so greatly stirred his imagination that he would refer to the effect even in his later years.

Entering the Central High School in Philadelphia at the earliest admissible age (thirteen years), chemistry and physics proved to be his favorite studies. He graduated in 1870 and was promptly made a member of the school staff, to teach chemistry. From that point started a career of scientific investigation, discovery, and invention that continued unremittingly until the advent of his final illness. In these teaching days he was greatly indebted also to the Franklin Institute, the laboratory and lecture room facilities of which afforded him many opportunities for satisfying his tastes. His death occurred on March 13, 1937, fifty-seven years after he left his post at the Central High School to enlarge his opportunities for discovery and invention and to take a leadership in manufacturing his own inventions.

Competent authority has entitled him a Modern Faraday. There was much of kin in the intellectual qualities of the two men, but their tastes led them along different creative paths. Michael Faraday was possessed with avidity to discover and explain the interrelations of phenomena of nature. Leaving to others the further investigations needed to apply his discoveries in devices of material utility for man, he extended his own researches among phenomena so that his discoveries are fundamental to a wide world of chemistry and physics,

and his name is a word to conjure with in circles where science is cultivated Elihu Thomson was interested in discovering relations of phenomena, but his avidity (contrary to that of Faraday) was for securing devices of utility for man from applications of his discoveries and also from already known factors in the field of science Being one who foresaw that (in material comforts) "Change may never change or pass away," to use Swinburne's phrase, Thomson pursued a fertile career primarily in invention, until his name became of world-wide fame in circles of engineering and notably of electrical engineering His temperament is illustrated by his own words expressed at a commemorative dinner held in 1930, "No greater joy has come to me than the joy of accomplishment Then, too, I have had the satisfaction of aiding in giving employment to large numbers of intelligent men and women "

Each of these two scientists contributed magnificently to human welfare and happiness, directly or indirectly Each deserves and has received world acclaim for his achievements The differences between their tastes and therefore between the scopes of their endeavors makes a more exact comparison impracticable as well as unnecessary

Elihu Thomson was one of the now rapidly disappearing generation of men who, by discoveries and inventions, wrought electrical engineering out of the early scientific foundations into the aspect of a great contribution to human comfort and happiness, and he was one of the greatest of that remarkable group His achievements have directly contributed so much to the comfort and thus to the happiness of men that the world owes him an inextinguishable debt

Thomson was elected a Fellow of this Academy on March 14, 1888, upon nomination of Charles R Cross, John Trowbridge, and Silas W Holman, honored professors of physics in Harvard and M I T , all now in their graves Accordant with his custom concerning scientific societies that attracted his interest and affection, he took lively part in Academy affairs, habitually attended the meetings, presented communications in 1900, 1910, 1912, 1919, 1922, 1933, and in 1928 wrote the Memoir of Professor Charles R Cross, one of his nominators He was a Member of Council, 1904-1908, Vice President 1908-1923, and Member of the Rumford Committee from 1903 until his death He was awarded the Rumford Medal in 1901 "for his inventions in electric welding and lighting "

The wide recognition of his work (especially during his later years) is indicated by his scientific society memberships and important medals conferred on him at home and abroad. It is said that no other man has been recipient of all three of the great British medals granted by great engineering and scientific associations. Few have ever received such a distinguished series of medals.

Honorary academic degrees of Ph D in 1894, Sc D in 1909 and LL D in 1924 have been conferred on him respectively by Tufts College, Harvard University and University of Pennsylvania, Victoria University, Manchester, England (his birthplace), conferred on him its degree of Sc D in 1924.

The importance of Thomson's work and the extent of its appreciation are well illustrated by the fullness of these various forms of recognition. The magnitude of his work of invention is indicated by the statement that over seven hundred patents have been issued covering inventions which he made. It is not appropriate here to make an enumeration, but those inventions have affected electrical engineering prodigiously. The earliest one of importance (made while he was still in Philadelphia) was the automatically regulating arc-light dynamo with three-coil spherical armature and blow-out arc-extinguisher at the commutator. This had great influence on the development of arc-lighting in the early days of electric lighting service. In the same early days he demonstrated in one experiment the reversibility of induction coils and the process of butt-welding by electric current. His manner of working and the meagreness of knowledge regarding electric circuits in those days are illustrated by a statement of Thomson reported by Dr C F Scott. "The Rhumkorff Coil" (said Thomson) "uses a low-voltage current for producing a very high voltage. I wondered if the process could be reversed and the high-voltage current in the fine winding would produce a current in the heavy winding. I was fearful of the results [i.e. to the coil] and put off experiments until I had a coil of my own. I placed the ends of the heavy terminals close together and observed carefully when the Leyden jars were discharged through the fine wire coil. There was a flash and when I attempted to separate the terminals I found them solidly welded together. That was the beginning of my work in electric welding." These observations contributed later to Professor Thomson establishing the extremely serviceable art of resistance

electric-welding and to his making important inventions in the field of electric transmission of power. Other observations in these Philadelphia days led to additional later important inventions.

When incandescent electric lighting was growing up, the art was at a disadvantage from lack of a simple registering meter comparable in qualities to a gas meter. Thomson's meter filled that gap and won for him the Paris Meter Prize in 1890 besides going into wide use. He produced lightning arresters for electric circuits with magnetic means for causing extinguishment of the sustained arc when the arrester operated in an electric power circuit. That "magnetic blowout" device has become so entwined in electrical engineering that its applications in electric circuits are innumerable. In his electric light and power developments he always gave great concern to the question of safety of the public and of users of the current. He was a leader in this direction of thought.

He early worked in the field of high-frequency currents and in the field of X-rays, with some discoveries and inventions in each, including the production of stereoscopic X-ray pictures. He discovered the repulsion forces caused by the magnetic effects of alternating currents acting on adjoining closed conducting circuits and utilized the phenomena in invented devices. And thus he went through the gamut of electrical affairs that attracted his attention and interest, nor did he wholly neglect the fields of chemistry and mechanical engineering.

He was happily married twice, once in 1884 with the issue of four children, and again in 1923. He had deep interest in children. His long-time and loyal secretary has said that he has frequently seen him "lose himself entirely in preoccupation with children's activities and it was always with great difficulty that we could revive his attention to some important matter, and then only with one eye cast eagerly in the direction of the children." He also was careful of the welfare of the young men who became his assistants, and many men who now are of importance in electrical engineering ascribe much of their success to their early relations with Professor Thomson. The adequacy and smooth sequences of his intellectual processes were always inspiring to young men.

He was devotedly interested in education to the end of his days and his relations with M I T and Harvard University were among his happiest. He became formally a lecturer in electrical engineering at

M I T in 1894 and so continued to the day of his death. He was elected a life member of its Corporation in 1898, was Acting President in 1920-1923 during an interregnum, and of late years was a member of the Executive Committee of the Corporation. From time to time he was member of Visiting Committees of departments such as electrical engineering, physics and other sciences. His devoted service to M I T and also to Harvard as a visitor and adviser, make education in science and engineering his debtor.

In addition to his absorbing professional occupation Professor Thomson took much interest in each new scientific phenomenon that came to his attention. A number of his brief articles published in Science or elsewhere related to such matters. He was a happy follower of several scientific avocations, principally as an amateur in astronomy, in music, and in color photography. For the former he built a small observatory on his place in Swampscott, Mass., in which was a modest telescope which he built for himself, even to the grinding of the lenses. He built for himself a pipe organ on which it was his pleasure to perform. And in his later years his wife was his congenial and perfect companion in the joys of color photography.

His personal characteristics were so admirably summed up at the Eightieth Birthday Dinner by Edwin W. Rice, Jr. (at first a student and then a life-long colleague of Thomson, than whom no man knew Thomson so well), that I quote his words "Throughout his whole career Professor Thomson has exhibited an unerring capacity for the selection of that thing or that process which was soundest and best, and simplicity and directness always characterized his designs. He seems to possess an intuitive insight into nature and her ways, probably because of the quickness and accuracy of his perception, combined with the depth and range of scientific knowledge, helped by a remarkably retentive memory. Difficulties never discourage him, but only stimulate him to greater endeavor. He has been a prolific inventor, a trained engineer and an inspiring teacher. Our generation has produced men who may have equalled or excelled him in some one of these fields, but no one has arisen in the generation who to such a superlative degree combined the quality of inventor, engineer and teacher."

DUGALD C. JACKSON

## CHARLES HOWARD WALKER (1857-1936)

Fellow in Class IV, Section 4, 1921

Charles Howard Walker was an architect and an educator. He was born in West Roxbury, January 9, 1857, and died April 12, 1936. His life as an architect began in 1875, when at the age of eighteen he entered the office of Sturgis and Brigham. Opportunities for work and study took him successively to New York in 1879 and in 1881 to Europe and Asia Minor. In 1885 he began the practice of architecture under his own name, later taking in Thomas Kimball as a partner. This partnership ended in 1899 after the Omaha Exposition for which the firm of Walker and Kimball were architects-in-chief. He practiced alone until 1911 when he took his son, Harold D. Walker, into the firm under the name of C. Howard Walker and Son. In 1925 the firm name became Walker and Walker and Kingsbury and in 1930 it was changed to Walker and Walker.

His work, which was as varied as his interests, as catholic as his tastes, covered a wide field ranging from domestic work of all sorts in and around Boston to Exposition Buildings at St. Louis and Omaha, from the Herald, Oliver Ditson, and Nile Buildings in Boston to the Second Church in Omaha—from such memorials as the War Memorial at Dedham or the John Boyle O'Reilly Monument in Boston to the entrance stairhall of the Boston Public Library, designed with McKim, Mead and White.

Walker's vigorous challenging mind, engaging personality and courageous support of his convictions won him increasing recognition among architects and laymen. His scholarship, for he was a profound student of the fine arts, his professional ability, his eloquence as a speaker won him appointments as lecturer at Harvard, the Massachusetts Institute of Technology, and the New England Conservatory of Music, gold medals from the American Institute of Architects, the Pennsylvania Academy, and the St. Louis and the Omaha Expositions, in addition to the degree of Doctor of Fine Arts from the University of Pennsylvania.

His death took from our midst a most vital, picturesque, and valiant spirit.

His was the privilege to love with so clear an insight that his criticism was only an incentive to greater effort. He differed violently

even with those dearest to him, and loved them the more that they withstood him His tenacity was only equalled by his generosity

For a younger generation he represented, not alone scholarly learning made vivid by personal reminiscence, but an essentially dynamic personality Contact with him shook the student out of his immature complacency, revealed how narrow were his theories, and how without foundation his convictions

The following lines from Browning's "Epilogue" were surely written to his measure

"One who never turned his back but marched breast forward,  
Never doubted clouds would break,  
Never dreamed, though right were worsted, wrong would  
triumph,  
Held we fail to rise, are baffled to fight better, sleep to wake "

WILLIAM EMFRSON

### WILLIAM MORTON WHEELER (1865-1937)

Fellow in Class II, Section III, 1900

William Morton Wheeler was born in Milwaukee, Wisconsin, 19 March 1865, and died suddenly in Cambridge, Massachusetts, on Patriots Day, 19 April 1937 Dr Wheeler's early life was spent in his native city Here he attended school, graduated from the German-American Normal College in 1884, and, after an absence of nearly a year at Ward's Natural Science Establishment in Rochester, New York, he served first as a teacher in the Milwaukee High School, 1885 to 1887, and then as Custodian of the newly established Milwaukee Public Museum, 1887 to 1890 In the autumn of 1890 he became Fellow and Assistant in Morphology under Dr C O Whitman at Clark University, Worcester, Massachusetts From Clark he removed with Dr Whitman to the newly established University of Chicago where as Instructor in Embryology and subsequently as Assistant Professor of that subject he remained from 1892 to 1899 As a preparation for this work, Wheeler spent the academic year of 1893-1894 abroad and studied at Würzburg, the Zoological Station at Naples, and at Liége After about six years at Chicago, he accepted the Professorship of Zoology at the University of Texas, Austin, Texas Here he remained till 1903 when he became Curator of Invertebrate

Zoology at the American Museum of Natural History in New York City. After five years of administrative work in the Museum, he returned to teaching by accepting the position of Professor of Economic Entomology at the Bussey Institution of Harvard University. Later, in 1926, he assumed the more appropriate title of Professor of Entomology and in 1934 he was made Professor of Entomology Emeritus. From 1915 to 1929 he was Dean of the Faculty of the Bussey Institution and from 1929 to 1937 he was Associate Curator of Insects in the Museum of Comparative Zoology.

Wheeler's early training in languages, which included beside Greek and Latin, the more important modern European tongues, stood him always in stead and his reading was extensive in breadth and voluminous in amount. By those who knew him best he was reported to be the most widely read member of his university. His reading included belles-lettres as well as science, in short all literature. As a result of his early thorough training in languages and his wide acquaintance with the printed word, his own style was unusually lucid and pungent. Few of his writings, even those of a purely technical character, are without literary turns that the reader will always take delight in recalling, and his more popular addresses, such as "The Termitoidea, or Biology and Society" (1920) and "The Dry-Rot of our Academic Biology" (1923), are replete with witty criticisms and comments that mark Wheeler a past master in his art. Of his three hundred and more publications the majority, as might be expected, are entomological in substance and most of these deal with that group of insects, the ants, which claimed his closest attention.

His eminence in biological science was recognized by election to membership in all the important biological societies in America and in many abroad. He was made a fellow of the American Academy of Arts and Sciences, March 10, 1909. He was a recipient of the Elliott Medal of the National Academy of Sciences in 1922 and of the Leidy Medal from the Philadelphia Academy of Natural Sciences in 1931. He served as Harvard Exchange Professor with France in 1925. He held honorary degrees from the University of Chicago, Harvard University, Columbia University, and the University of California. The French Republic made him an Officer in the Legion of Honor. He took great pleasure in the distinctions bestowed upon him, but these honors never disturbed his unassuming demeanor and his native modesty.

Wheeler is too near the present generation to allow any one to form an estimate of his genius, for genius he had in the fullest sense. As a man of scientific letters, he was supreme. He was possessed of extraordinary knowledge. His sincerity was beyond reproach. To paraphrase from a recent tribute to him, he was a great experience in the lives of those who knew him, and his departure leaves a void that nothing can fill.

Dr Wheeler was survived by all his immediate family, his wife, Mrs Dora Emerson Wheeler, his son, Dr Ralph Emerson Wheeler, and his daughter, Miss Adeline Wheeler.

GEORGE HOWARD PARKER

### FRANCIS HENRY WILLIAMS (1852-1936)

Fellow in Class II, Section 4, 1902

Francis Henry Williams, son of Henry Willard and Elizabeth (Dewe) Williams, was born in Uxbridge, Mass., October 15, 1852. He early evinced a love of scientific study, and entered the Massachusetts Institute of Technology in 1869, graduating in 1873 with the degree of Bachelor of Science in Chemistry. His scientific interests were not confined to chemistry, however, for the following year he served as assistant on the United States Transit of Venus Expedition to Japan, and on the completion of this work continued his travels on a tour around the world. On returning home in 1875 he entered the Harvard Medical School and received his M.D. degree in 1877. This was followed by two years of additional medical study in Europe, notably in Vienna and Paris. In 1879 he began his long and exceptionally useful practice in Boston. In 1884 he was appointed Instructor in Materia Medica and in 1885 Assistant Professor of Materia Medica and general Therapeutics at the Harvard Medical School, an association which he maintained until 1891. For twenty years, from 1883 to 1913 he was connected with the Boston City Hospital, first as Physician to the Out Patient Department, and from 1896 to 1913 as Visiting Physician. In 1913 he was made Senior Physician, a post of honor which he held for many years.

Dr Williams' service to medicine was of great significance. In 1892 he initiated the taking of cultures from the throat in suspected diphtheria cases, and their bacteriological examination, a procedure

which is now universal in well-ordered city health departments, and in 1894 he was the first in this community to use antitoxin in the treatment of the disease. Important as were these procedures, Dr. Williams will be especially remembered for those epoch-making investigations on X-rays begun in 1896 at the City Hospital and in the laboratory of physics at the Massachusetts Institute of Technology, for he insisted on exact knowledge of the science he applied as well as delicacy in the control of its application in diagnosis or therapeutic use. His theoretical work coupled with his extensive application in the diagnosis of thoracic conditions, and later in investigations of the alimentary tract, made him the leader in the use of this new tool in medicine. His extensive and exhaustive studies led to the publication of his book "The Roentgen Rays in Medicine and Surgery," the ~~first~~ edition of which appeared in 1901. This was the original monograph on clinical radiology produced in America, and so authoritative that two later editions were soon demanded. He was among the first to recognize the damage caused by repeated dosages of X-rays on living tissue, and adopted protective devices for his patients and himself. He also devised and built with the cooperation of his brother-in-law, Dr. William Rollins, several new types of equipment, including a 7-foot static machine for use in X-ray application.

After the discovery of radium in 1898, Dr. Williams turned his attention to its possibilities in the treatment of disease. With characteristic thoroughness he visited Paris and conferred with the Curies. By 1900 he had developed original methods for the treatment of certain diseases by the use of beta rays from radium, especially some types of diseased tonsils (thus making operation unnecessary) and many diseases of the eye. His work was always carried on with most scrupulous accuracy of measurement, and he always emphasized the necessity that the physician should know the dangers that might accrue from failure to observe with absolute accuracy the potency of the rays used. His first paper on the use of radium was published in 1904, on "Some Physical Properties and Medical Uses of Radium Salts," and contained a record of 42 cases treated with radium bromide. In all his publications, which were numerous, and in his verbal statements he cautioned against use of radium salts without due discrimination or absolute control of dosages. Again his inventive genius, in cooperation with Dr. Rollins, brought into existence numerous

devices for exact measurement of rays and particles, and equipment for use in the study and treatment of certain maladies which might be combatted by use of this new curative agent. Radiology owes much to him, for he was a scientific pioneer whose discoveries were given to the profession freely with no thought of personal advantage.

Dr Williams married in 1891 Miss Anna Dunn Phillips of Boston, a lady of many charitable and philanthropic interests. Her death preceded that of Dr Williams by about a year. There were no children.

Dr Williams was widely known in scientific associations. He was not only a Fellow of this Academy, but of the American Association for the Advancement of Science, and a member of the American Medical Association, the Massachusetts Medical Society, and the Société de Radiologie Médicale de France, and the Association of American Physicians of which he was president in 1917-18. His honorary and corresponding memberships included the K K Gesellschaft der Aerzte of Vienna, American Radium Society, American Roentgen Society, and the Radiological Society of North America.

One other phase of Dr Williams' life is worthy of record,—his long association with and great loyalty to the Massachusetts Institute of Technology. He was elected to life membership in its Corporation in 1882, and was a member of its Executive Committee for more than 25 years, and also served for a long period as Secretary of the Corporation. His services as a member of the Visiting Committee on its Departments of Biology and Chemistry were characterized by keen insight and inquiry into the needs and aims of the department, and he was most helpful and generous in his efforts to advance scientific work. For more than fifty years his devotion to his Alma Mater was of the highest type whether in days of great poverty and danger, or in later times when its expansion and continued efficiency were assured by friends and Alumni.

In his personal qualities Dr Williams was also remarkable. His appearance always commanded attention, not only because of his height, carriage, and a fineness and intellectuality of countenance, but also because he was always an example of kindly dignity and true courtesy.

He had a deep appreciation of science and the arts, and a keen sense of humor, and while reticent and unaggressive, possessed a

warm spirit of friendliness and companionship. In a word, he was a fine exponent of scientific medicine, a true investigator, and above all, a cultured gentleman faithful always to his ideals of professional action and of human relations.

S C PRESCOTT

### JAMES HAUGHTON WOODS (1864-1935)

Fellow in Class IV Section I 1914

James Haughton Woods was born in Boston, November 27, 1864, son of Joseph Wheeler Woods and Caroline Frances Fitz. His inheritance on either side might have indicated his bent toward teaching or the ministry, but the breadth of his interests and his erudition, especially in Oriental languages, literatures, and philosophies, gave him a unique place among American scholars. At the time of his death in Tokyo (January 13, 1935), he was engaged in the study of manuscripts of the Tendai sect of Japanese Buddhism which had been left to his editing by William Sturgis Bigelow, long resident in Japan. He was preparing for publication a translation of the *Visuddhi-Magga*, an important Cinghalese source for southern Buddhism. He had some knowledge of at least fifteen languages, most of them tools for his Oriental studies, and in this field he was particularly occupied with the difficult bit of history in which Buddhism, passing from India into Thibet and China, assumed the several Mahayana forms now found in China and Japan.

Preparation for his life work was broad and long-continued. During fifteen years after his graduation from Harvard in 1887, he was chiefly occupied with studies in Europe and America, in classical languages, the philosophies of Greece and India, theology, anthropology, Sanskrit and Indic Philology (under Lanman). He received the degree of Ph.D. in philosophy at Strassburg in 1896. It was in 1902 that his interests took their definitive turn. Advised by Lanman and William James, he spent some time in the spring of that year with Deussen, at Kiel, and then proceeded to India, where he spent a year in Kashmir and at Benares, the first of several visits to the Orient.

In the fall of 1903 he became instructor in philosophy at Harvard, dealing with the philosophical systems of India. He remained a member of the department of philosophy until his retirement in 1934.

During this time he was thrice chairman of the department, and twice exchange professor at the Sorbonne.

His published work was almost entirely in the field of Indian philosophies, the Vedanta, the Yoga, and Buddhism,—translations, commentaries, editions of texts. Among his translations are to be mentioned *The Yoga System of Patanjali* (1914), *Mani-Prabha* (1915), and the *Isuddhi-magga*, awaiting publication. He collaborated with D. Kosambi (Bombay) in preparing for the Pali Text Society an edition of the first part of *Papaneasudam*, an important commentary on the *Majjhima Nikaya*.

He was married in 1907 to Gertrude Baldwin, who died in 1926, and in 1927 to Elizabeth Robinson, who survives him.

Wood's life was one of distinguished effectiveness in fields of difficult endeavor, requiring infinite patience and persistence as well as discernment and sympathy. His power was carried with great quietness and modesty. He was not fluent in vocal expression, he was rather silent, except for his laugh which at once revealed the hearty simplicity of his spirit, always easily approachable but not widespread in social relationships, he was deep and loyal in his friendships, which included men in all parts of the world. He did much to maintain the strength of the department of philosophy at Harvard, and to build up the Harvard-Yenching Foundation of which he was a trustee from 1928 onward. He left a lasting mark on students and colleagues, not more by his learning and the wholly fresh interpretations he was able to give of the traditions of Asia, than by the personal affection which he gave and inspired, and which followed him with tributes both in this country and in the Orient.

W E HOCKING



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34 Leighton Bruerton Smith	Beverly
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34 Chester Laurens Dawes	Cambridge
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20 Theodore Harwood Dillon	Brookline
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22 Gano Dunn	New York, N.Y.
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32 Albert Haertlein	Watertown
36 Murray Philip Horwood	Newton Center
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34 Jerome Clarke Hunsaker	Boston
23 James Robertson Jack	Watertown
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16 Isaiah Bowman	Baltimore, Md
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29 Kirk Bryan	Cambridge
33 Frank Morton Carpenter	Newtonville
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09 Reginald Aldworth Daly	Cambridge
34 Sterling Price Fergusson	Milton
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17 James Walter Goldthwait	Hanover, N H
14 Louis Caryl Graton	Cambridge
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21 William Jackson Humphreys	Washington, D C
16 Ellsworth Huntington	New Haven, Conn
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30 Karl Sax	Jamaica Plain
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32 Elliott Carr Cutler	Brookline
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32 Fred Bates Lund	Newton
33 George Burgess Magrath	Boston
13 Frank Burr Mallory	Brookline
21 William James Mayo	Rochester, Minn
34 Leroy Matthew Simpson Miner	Newtonville
26 George Richards Minot	Brookline
28 William Lorenzo Moss	Augusta, Ga
28 John Howard Mueller	West Roxbury
25 Robert Bayley Osgood	Boston
37 Walter Walker Palmer	New York, N Y
27 Joseph Hershey Pratt	Boston
35 Tracy Jackson Putnam	Brookline
34 William Carter Quinby	Brookline
34 Arthur Hiler Ruggles	Providence, R. I
27 Andrew Watson Sellards	Boston
33 George Cheever Shattuck	Brookline
30 Torald Hermann Sollmann	Cleveland, Ohio
21 Charles Wardell Stiles	Washington, D. C
14 Richard Pearson Strong	Boston
30 Fritz Bradley Talbot	Brookline
14 Ernest Edward Tyzzer	Wakefield

14 Frederick Herman Verhoeff	Brookline
27 Joseph Treloar Wearn	Cleveland, Ohio
33 Soma Weiss	Cambridge
25 Benjamin White	New York, N Y
12 Simeon Burt Wolbach	South Sudbury
23 Hans Zinsser	Boston

CLASS III—*The Social Arts*—152SECTION I—*Jurisprudence*—38

(24) 32 Francis Noyes Bulch	Jamaica Plain
06 Joseph Henry Beale	Cambridge
36 Stoughton Bell	Cambridge
33 Harry Augustus Bigelow	Chicago, Ill
33 Henry Wolf Biklé	Philadelphia, Pa
36 Wilfred Bolster	Brookline
36 Claude Raymond Branch	Providence, R I
33 Benjamin Nathan Cardozo	Washington, D C
33 John Dickinson	Washington, D C
31 Fred Tarbell Field	Newton
32 Felix Frankfurter	Cambridge
30 Thomas Hovey Gage	Worcester
33 Theodore Francis Green	Providence, R I
32 Walter Perley Hall	Fitchburg
33 Learned Hand	New York, N Y
18 Charles Evans Hughes	Washington, D C
31 Nathan Isaacs	Cambridge
21 Frederick Lawton	Boston
32 Sayre Macneil	Azusa, Cal
32 Calvert Magruder	Cambridge
31 William DeWitt Mitchell	New York, N Y
31 Edmund Morris Morgan	Arlington
31 Herbert Parker	South Lancaster
36 Philip Stanley Parker	Brookline
36 Henry Parkman, Jr	Boston
01 George Wharton Pepper	Philadelphia, Pa
11 Roscoe Pound	Watertown
36 Stanley Elroy Qua	Lowell
12 Arthur Prentiss Rugg	Worcester

32 Francis Bowes Sayre	Washington, D C
21 Austin Wakeiman Scott	Cambridge
35 James Brown Scott	Washington, D C
36 Sidney Post Simpson	Cambridge
33 Harlan Fiske Stone	Washington, D. C
32 Edward Sampson Thurston	Cambridge
14 Eugene Wambaugh	Cambridge
37 Joseph Warren	Brookline
(28) 32 Edmund Allen Whitman	Cambridge

**CLASS III, SECTION II—*Government, International Law, and Diplomacy*—26**

36 Howard Landis Bevis	Cambridge
33 Edwin Montefiore Borchard	New Haven, Conn
32 William Richards Castle, Jr	Washington, D C
32 Joseph Perkins Chamberlain	New York, N Y
33 Robert Treat Crane	New York, N Y
35 Tyler Dennett	
31 Sidney Bradshaw Fay	Cambridge
27 William Cameron Forbes	Norwood
34 Edgar Stephenson Furniss	New Haven, Conn
32 Joseph Clark Grew	Tokyo, Japan
35 Charles Grove Haines	Los Angeles, Cal
16 Albert Bushnell Hart	Cambridge
27 Arthur Norman Holcombe	Cambridge
31 Manley Ottmer Hudson	Cambridge
32 Philip Caryl Jessup	New York, N Y
36 Morris Bryan Lambie	Cambridge
97 Abbott Lawrence Lowell	Boston
18 William MacDonald	New York, N. Y
32 Charles Edward Merriam	Chicago, Ill
19 John Bassett Moore	New York, N Y
13 William Bennett Munro	Pasadena, Cal
27 Westel Woodbury Willoughby	Washington, D. C.
32 William Franklin Willoughby	Washington, D. C.
14 George Grafton Wilson	Cambridge
27 Quincy Wright	Chicago, Ill.
33 Henry Aaron Yeomans	. Cambridge

CLASS III, SECTION III—*Economics and Sociology*—62

36 James Waterhouse Angell	New York, N Y
36 James Cummings Bonbright	New York, N Y
33 Harold Hitchings Burbank	Cambridge
36 Philip Cabot	Milton
36 Edward Hastings Chamberlin	Cambridge
16 John Bates Clark	New York, N Y
34 John Maurice Clark	Westport, Conn
28 Arthur Harrison Cole	Cambridge
31 Melvin Thomas Copeland	Cambridge
31 William Leonard Crum	Cambridge
32 William James Cunningham	Cambridge
34 Winthrop More Daniels	Saybrook Point, Conn
21 Clive Day	New Haven, Conn
13 Davis Rich Dewey	Cambridge
32 Arthur Stone Dewing	Newton
32 Wallace Brett Donham	Boston
34 John Franklin Ebersole	Belmont
36 Fred Rogers Fairchild	New Haven, Conn
36 Frank Albert Fetter	Princeton, N J
12 Irving Fisher	New Haven, Conn
31 James Ford	Cambridge
34 Ralph Evans Freeman	Cambridge
13 Edwin Francis Gay	Pasadena, Cal
33 Sheldon Glueck	Cambridge
34 Robert Murray Haig	New York, N Y
32 Henry Wyman Holmes	Cambridge
34 Edwin Walter Kemmerer	Princeton, N J
34 Frank Hyneman Knight	Chicago, Ill
36 Roswell Cheney McCrea	New York, N Y.
34 Robert Morison MacIver	New York, N Y
32 Walter Wallace McLaren	Williamstown
36 Malcolm Perrine McNair	Cambridge
32 Leon Carroll Marshall	Chevy Chase, Md.
33 Edward Sagendorph Mason	Cambridge
36 Elton Mayo	Cambridge
34 Richard Stockton Meriam	South Lincoln
34 Harry Alvin Mills	Chicago, Ill

32	Frederick Cecil Mills	New York, N Y
31	Wesley Clair Mitchell	New York, N Y
34	Arthur Eli Monroe	Cambridge
32	Harold Glenn Moulton	Washington, D C
34	Edwin Griswold Nourse	Washington, D C
32	William Fielding Ogburn	Chicago, Ill
33	Robert Ezra Park	Chicago, Ill
32	Leo S Rowe	Washington, D C
37	Clyde Orval Ruggles	Cambridge
36	Thomas Henry Sanders	Cambridge
33	Josef Alois Schumpeter	Cambridge
32	Carl Snyder	New York, N Y
31	Pitirim Alexandrovich Sorokin	Winchester
31	Olver Mitchell Wentworth Sprague	Cambridge
[89] 01	Frank William Taussig	Cambridge
34	Frederick John Teggart	Berkeley, Cal
33	William Isaac Thomas	New York, N Y
37	Harry Rudolph Tosdal	Belmont
31	Donald Skeele Tucker	Belmont
33	Abbott Payson Usher	Cambridge
34	Jacob Viner	Chicago, Ill
32	John Henry Williams	Cambridge
36	Joseph Henry Willits	Swarthmore, Pa
34	Leo Wolman	New York, N Y.
34	Carle Clark Zimmerman	Winchester

CLASS III, SECTION IV—*Administration and Affairs*—26

(25) 32	Charles Francis Adams	Concord
(25) 32	Charles Foster Batchelder	Cambridge
32	Henry Sturgis Dennison	Framingham
(28) 32	William Lusk Webster Field	Milton
16	Frank Johnson Goodnow	Baltimore, Md
35	Jerome Davis Greene.	Cambridge
(28) 32	Edward Jackson Holmes	Boston
34	Matt Bushnell Jones	Newton Center
34	Henry Plumpton Kendall	Walpole
(27) 32	Nathaniel Thayer Kidder	Milton
32	Thomas William Lamont	New York, N Y

34 Clarence Cook Little	Bar Harbor, Me
36 Dumas Malone	Cambridge
33 James Vance May	Boston
(24) 32 Andrew James Peters	Jamaica Plain
02 Herbert Putnam	Washington, D C
(28) 32 Alfred Lawrence Ripley	Andover
34 Erwin Haskell Schell	Cambridge
35 Henry Lee Shattuck	Boston
37 Henry Southworth Shaw	Exeter, N H
(28) 32 Payson Smith	Brookline
33 Albert Warren Stearns	Billerica
(25) 32 Charles Henry Taylor	Boston
36 Clair Elsmere Turner	Arlington
(24) 32 Edwin Sibley Webster	Brookline
(25) 32 Benjamin Loring Young	Weston

CLASS IV—*The Humanities*—193SECTION I—*Theology, Philosophy, and Psychology*—49

32 Michael Joseph Ahern	Weston
33 Gordon Willard Allport	Cambridge
32 James Rowland Angell	New Haven, Conn
33 John Gilbert Beebe-Center	Swampscott
24 Edwin Garrigues Boring	Cambridge
28 Edgar Sheffield Brightman	Newton
31 Henry Addington Bruce	Cambridge
32 Leonard Carmichael	Rochester, N Y
36 Robert Pierce Casey	Providence, R I
33 J[ames] McKeen Cattell	Garrison, N Y
28 Walter Fenno Dearborn	Cambridge
18 Edmund Burke Delabarre	Providence, R I
24 Raymond Dodge	Tryon, N C
33 Curt John Ducasse	Providence, R I
37 Clarence Henry Graham	Providence, R I
30 William Henry Paine Hatch	Cambridge
32 William Healy	Boston
10 Wilham Arthur Heidel	Middletown, Conn.
21 William Ernest Hocking	Cambridge
35 Clark Leonard Hull	New Haven, Conn.

33	Walter Samuel Hunter	Providence, R. I.
17	Frederick John Foakes Jackson	Englewood, N. J.
28	Albert Cornelius Knudson	Cambridge
34	Kurt Koffka	Northampton
32	Karl Spencer Lashley	Belmont
13	William Lawrence	Boston
29	Clarence Irving Lewis	Lexington
33	Lee Sullivan McCollester	Tufts College
22	William McDougall	Durham, N. C.
10	Edward Caldwell Moore	Cambridge
35	Henry Alexander Murray, Jr.	Boston
32	Arthur Darby Nock	Cambridge
32	William Cardinal O'Connell	Boston
28	Johnson O'Connor	Boston
17	Charles Edward Park	Boston
18	Leighton Parks	London, England
33	Carroll Cornelius Pratt	New Brunswick, N. J.
30	James Hugh Ryan	Omaha, Neb.
31	Henry Knox Sherrill	Boston
27	Willard Learoyd Sperry	Cambridge
29	Russell Henry Stafford	Brookline
34	Lewis Madison Terman	Stanford University, Cal.
34	Edward Lee Thorndike	New York, N. Y.
37	Louis Leon Thurstone	Chicago, Ill.
28	Henry Bradford Washburn	Cambridge
17	John Broadus Watson	New York, N. Y.
33	Frederic Lyman Wells	Newton Highlands
35	Robert Sessions Woodworth	New York, N. Y.
15	Robert Mearns Yerkes	New Haven, Conn.

**CLASS IV, SECTION II—History, Archaeology, and Anthropology—38**

18	Charles McClean Andrews	New Haven, Conn.
28	James Phinney Baxter, 3d	Williamstown
23	Carl Lotus Becker	Ithaca, N. Y.
27	Robert Pierpont Blake	Cambridge
12	Franz Boas	New York, N. Y.
(25) 32	William Brooks Cabot	Boston
34	Clarence Gordon Campbell	New York, N. Y.

12 George Henry Chase	Cambridge
21 Max Farrand	San Marino, Cal
21 William Scott Ferguson	Cambridge
10 Worthington Chauncey Ford	Cambridge
33 Henry Thatcher Fowler	Providence, R I
18 Evarts Boutell Greene	New York, N Y
19 Charles Downer Hazen	New York, N Y
14 Bert Hodge Hill	Athens, Greece
27 Earneat Albert Hooton	Cambridge
33 Halford Lancaster Hoskins	Tufts College
15 Aleš Hrdlicka	Washington, D C
12 Alfred Louis Kroeber	Berkeley, Cal
15 Kirzopp Lake	Haverford, Pa
22 George LaPiana	Cambridge
32 Waldo Gifford Leland	Washington, D C
20 Charles Howard McIlwain	Belmont
14 Roger Bigelow Merriman	Cambridge
15 Samuel Eliot Morison	Boston
34 Robert Henry Pfeiffer	Cambridge
14 George Andrew Reisner	Boston
34 David Moore Robinson	Baltimore, Md
23 Michael Ivanovich Rostovtzeff	New Haven, Conn
33 Edward Sapir	New Haven, Conn.
27 George Sarton	Cambridge
36 Donald Scott	Cambridge
34 Theodore Leslie Shear	Princeton, N J
26 Herbert Joseph Spinden	Brooklyn, N Y
32 Charles Holt Taylor	Cambridge
11 Charles Cutler Torrey	New Haven, Conn
11 Alfred Marston Tozzer	Cambridge
20 Clark Wissler	New York, N Y

CLASS IV, SECTION III—*Philology*—56

31 Edward Cooke Armstrong	Princeton, N. J
33 William Nickerson Bates	Philadelphia, Pa
35 Charles Henry Beeson	Chicago, Ill
33 Campbell Bonner	Ann Arbor, Mich.
35 Robert Johnson Bonner	Chicago, Ill

33	Carleton Brown	New York, N. Y
21	Carl Darling Buck	Chicago, Ill
18	Edward Capps	Princeton, N. J.
20	Walter Eugene Clark	Cambridge
32	Ronald Salmon Crane	Chicago, Ill
32	Morris William Croll	Princeton, N. J.
31	Samuel Hazzard Cross	Cambridge
20	Franklin Edgerton	New Haven, Conn.
21	Frank Edgar Farley	Middletown, Conn.
14	Jeremiah Denis Mathias Ford	Cambridge
35	Tenney Frank	Baltimore, Md.
30	James Geddes, Jr.	Brookline
13	Charles Hall Grandgent	Cambridge
16	Louis Herbert Gray	New York, N. Y.
25	Wilham Chase Greene	Cambridge
13	Charles Burton Gulick	Cambridge
19	Roy Kenneth Hack	Cincinnati, Ohio
34	Austin Morris Harmon	New Haven, Conn.
31	Raymond Dexter Havens	Baltimore, Md.
18	George Lincoln Hendrickson	New Haven, Conn.
17	William Guild Howard	Cambridge
21	Eugene Xavier Louis Henry Hyvernat	Washington, D. C.
15	Carl Newell Jackson	Cambridge
13	James Richard Jewett	Cambridge
32	(Ralph) Hayward Keniston	Chicago, Ill.
34	Roland Grubb Kent	Philadelphia, Pa.
98	George Lyman Kittredge	Cambridge
33	Hans Kurath	Providence, R. I.
32	Ernest Felix Langley	Cambridge
[81] 98	Charles Rockwell Lanman	Cambridge
33	Ivan Mortimer Linforth	Berkeley, Cal.
11	Albert Matthews	Boston
35	Benjamin Dean Meritt	Princeton, N. J.
28	William Albert Nitze	Chicago, Ill.
32	George Rapall Noyes	Berkeley, Cal.
34	Wilham Abbott Oldfather	Urbana, Ill.
33	Howard Rollin Patch	Northampton
32	Arthur Stanley Pease	Cambridge

35	Henry Washington Prescott	Chicago, Ill
13	Edward Kennard Rand	Cambridge
11	Fred Norris Robinson	Cambridge
31	Robert Kilburn Root	Princeton, N J
35	Henry Arthur Sanders	Ann Arbor, Mich
18	Rudolph Schevill	Berkeley, Cal
32	Horatio Elwin Smith	New York, N Y
89	Franklin Bache Stephenson	Washington, D C
32	William Thomson	Cambridge
33	George Benson Weston	Cambridge
30	Ernest Hatch Wilkins	Oberlin, Ohio
33	Harry Austryn Wolfson	Cambridge
33	Karl Young	New Haven, Conn

CLASS IV, SECTION IV—*The Fine Arts and Belles Lettres*—50

31	Stephen Vincent Benét	New York, N Y
26	Frank Weston Benson	Salem
32	(William) Welles Bosworth	New York, N Y
33	John Alden Carpenter	Chicago, Ill
32	Chalmers Dancy Clifton	New York, N Y
33	Charles Collens	Newton Center
32	Kenneth John Conant	Cambridge
34	Charles Jay Connick	Newtonville
29	Charles Townsend Copeland	Cambridge
[17] 30	Ralph Adams Cram	Boston
33	Cyrus Edwin Dallin	Arlington Heights
34	Samuel Foster Damon	Providence, R I
32	George Harold Edgell	Cambridge
21	William Emerson	Cambridge
33	Carl Engel	New York, N Y
30	John Erskine	New York, N Y
10	Arthur Fairbanks	Hanover, N H
18	Edward Waldo Forbes	Cambridge
31	Robert Frost	South Shaftsbury, Vt
27	Wallace Goodrich	Boston
14	Robert Grant	Boston
36	Wilham Clifford Heilman	Cambridge
29	Edward Burlingame Hill	Boston

31 Robert Silliman Hillyer	. Cambridge
27 Charles Hopkinson	Manchester
12 Mark Antony DeWolfe Howe	Boston
18 Archer Milton Huntington	New York, N Y
31 Henry James	New York, N Y
(25) 32 William James	Cambridge
33 Leo Rich Lewis	Tufts College
20 John Ellerton Lodge	Washington, D C
21 John Livingston Lowes	Cambridge
21 Charles Donagh Maginnis	Brookline
31 Paul Manship	New York, N Y.
31 Daniel Gregory Mason	New York, N Y
31 Frank Jewett Mather	Washington Crossing, Pa
31 Kenneth Ballard Murdock	Cambridge
14 William Allan Neilson	Northampton
28 Curtis Hidden Page	Gilmanton, N H
21 William Lyon Phelps	New Haven, Conn
(24) 32 Anthony John Philpott	Arlington
21 Chandler Rathfon Post	Cambridge
22 Paul Joseph Sachs	Cambridge
14 Ellery Sedgwick	Boston
19 Henry Dwight Sedgwick	Dedham
33 David Stanley Smith	Woodbridge, Conn
35 Walter Raymond Spalding	Cambridge
27 Edmund C Tarbell	New Castle, N H
14 Owen Wister	Philadelphia, Pa
22 Charles Henry Conrad Wright	Cambridge

## FOREIGN HONORARY MEMBERS—112

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CLASS I—*Mathematical and Physical Sciences*—31SECTION I—*Mathematics and Astronomy*—9

22 Sir Arthur Stanley Eddington	Cambridge, England
34 Ronald Aylmer Fisher	Harpden, Herts
20 Jacques Salomon Hadamard	Paris
21 Godfrey Harold Hardy	Cambridge, England
27 Ejnar Hertzsprung	Leyden
17 Tullio Levi-Civita	Rome
03 Charles Émile Picard	Paris
15 Charles Jean de la Vallée Poussin	Louvain
29 Hermann Weyl	Princeton, N. J.

CLASS I, SECTION II—*Physics*—8

29 Vilhelm Frimann Koren Bjerke	Oslo
24 Albert Einstein	Princeton, N. J.
29 James Franck	Baltimore, Md.
29 Abram F. Joffé	Leningrad
03 Sir Joseph Larmor	Cambridge, England
28 Friedrich Paschen	Charlottenburg
14 Max Planck	Berlin
02 Sir Joseph John Thomson	Cambridge, England

CLASS I, SECTION III—*Chemistry*—7

29 Johannes N. Brønsted	Copenhagen
27 Peter Debye	Berlin
33 Jaroslav Heyrovský	Prague
33 Fritz Paneth	London
28 Søren Peter Laurits Sørensen	Copenhagen
29 Heinrich Wieland	Munich
34 Richard Willstätter	Munich

CLASS I, SECTION IV—*Technology and Engineering*—7

36 Edward Victor Appleton	London
34 Luigi Lombardi	Rome

25 Maurice d'Ocagne	Paris
29 Ludwig Prandtl	Göttingen
29 Emil Probst	Karlsruhe
29 Aurel Stodola	Zürich
31 Karl Willy Wagner	Berlin

**CLASS II—Natural and Physiological Sciences—29**

**SECTION I—Geology, Mineralogy, and Physics of the Globe—9**

17 Frank Dawson Adams	Montreal
[15] 19 Charles Barrois	Lille
36 Raoul Blanchard	Grenoble, France
14 Waldemar Christofer Brogger	Oslo
29 Léon Wilham Collet	Geneva
34 Arthur Holmes	Durham
22 Emmanuel de Margerie	Paris
21 Gustaf Adolf Frederik Molengraaff	Delft
18 Sir William Napier Shaw	London

**CLASS II, SECTION II—Botany—6**

32 Frederick Orpen Bower	Ripon
31 Ludwig Diels	Berlin
32 Kihgo Miyabe	Sapporo, Japan
29 Otto Renner	Jena
32 Sir Albert Charles Seward	London
35 Sir William Wright Smith	Edinburgh

**CLASS II, SECTION III—Zoology and Physiology—7**

20 Maurice Caullery	Paris
34 Archibald Vivian Hill	London
31 August Krogh	Copenhagen
30 Louis Édouard Lapicque	Paris
28 Charles Tate Regan	London
33 Hans Spemann	Freiburg : Br
28 Sir D'Arcy Wentworth Thompson	St Andrews

**CLASS II, SECTION IV—Medicine and Surgery—7**

18 Sir Thomas Barlow, Bart	London
27 Sir Henry Hallett Dale	London

33 Sir Arthur Keith	London
28 Mikinosuke Miyajima	Tokyo
27 Friedrich von Müller	Munich
18 Sir Charles Scott Sherrington	Ipswich, England
36 (Jean) Hyacinthe Vincent	Paris

CLASS III—*The Social Arts*—21SECTION I—*Jurisprudence*—6

27 Léon Duguit	Bordeaux
33 François Geny	Nancy
33 Hans Kelsen	Vienna
33 Juliusz Makarewicz	Lwów
33 Rudolph Stammle	Wernigerode a H
33 Giorgio Del Vecchio	Rome

SECTION II—*Government, International Law, and Diplomacy*—2

32 Paul Claudel	Paris
32 Hu Shih	Peiping

SECTION III—*Economics and Sociology*—11

32 Arthur Lyon Bowley	Haslemere, Surrey
34 Gustav Cassel	Djursholm, Sweden
35 Luigi Einaudi	Turin
32 Ralph George Hawtrey	London
35 John Maynard Keynes	Cambridge, England
35 René Maunier	Paris
28 Arthur Cecil Pigou	Cambridge, England
32 Charles Rist	Fraisses (Loire)
33 Werner Sombart	Berlin
35 S Rudolph Steinmetz	Amsterdam
34 Peter B Struve	Belgrade

SECTION IV—*Administration and Affairs*—2

33 Gösta A Bagge	Stockholm
33 Sir Josiah Stamp	Shortlands, Kent

CLASS IV—*The Humanities*—31SECTION I—*Theology, Philosophy, and Psychology*—8

36 Miguel Asín y Palacios	Madrid
28 Henri Louis Bergson	Paris
28 Benedetto Croce	Naples
29 Étienne Gilson	Melun
28 Edmund Husserl	Freiburg i B
32 Pierre Janet	Paris
28 Wolfgang Kohler	Berlin
37 Henri Pieron	Paris

SECTION II—*History, Archaeology, and Anthropology*—9

33 Rafael Altamira y Crevea	Madrid
36 Marcel Aubert	Paris
29 Godfrey Rathbone Benson, Baron Charnwood	London
97 Wilhelm Dörpfeld	Berlin-Lichterfelde
31 Rt Hon Herbert Albert Laurens Fisher	Oxford
33 Friedrich Meinecke	Berlin-Dahlem
22 Henri Pirenne	Uccle-Brussels
30 Sir Aurel Stein	Srinagar, Kashmir
31 George Macaulay Trevelyan	Cambridge, England

SECTION III—*Philology*—7

29 Joseph Bédier	Paris
09 Hermann Georg Jacobi	Bonn
36 Paul Kretschmer	Vienna
32 Paul Mazon	Paris
[12] 28 Hanns Oertel	Munich
17 Ramón Menéndez Pidal	Madrid
32 Frederick William Thomas	Oxford

SECTION IV—*The Fine Arts and Belles Lettres*—7

30 Alfredo Casella	Rome
23 Henry Guy	Grenoble
29 Paul Hazard	Paris
34 Serge Koussevitzky	Paris and Boston
27 Gilbert Murray	Oxford
31 Edgar Allison Peers	Liverpool
27 Henri Rabaud	Paris

## ALPHABETICAL INDEX TO LISTS OF MEMBERS

The letters F and FHM refer to the lists of Fellows and Foreign Honorary Members, respectively. The class and section are indicated by the numerals following.

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| Abbot, C G           | F, I 1     | Bard, P           | F, II 3    |
| Abrams, L. R         | F, II 2    | Barlow, Sir T     | FHM, II 4  |
| Adams, C A           | F, I 4     | Barnett, S J      | F, I 2     |
| Adams, C F           | F, III 4   | Barrois, C        | FHM, II 1  |
| Adams, C R           | F, I 1     | Barrows, H K      | F, I 4     |
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| Ahern, M J           | F, IV 1    | Beale, J H        | F, III 1   |
| Altamira y Crevea, R | FHM, IV 2  | Beattie, J A      | F, I 3     |
| Allport, G W         | F, IV 1    | Becker, C L       | F, IV 2    |
| Ames, A, Jr          | F, I 2     | Béhier, J         | FHM, IV 3  |
| Ames, J S            | F, I 2     | Beebe-Center, J G | F, IV 1    |
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| Anderson, E.         | F, II 2    | Bell, S           | F, III 1   |
| Andrews, C M         | F, IV 2    | Benedict, F G     | F, II 3    |
| Angell, J R          | F, IV 1    | Benét, S V        | F, IV 4    |
| Angell, J W          | F, III 3   | Bennett, A A      | F, I 1     |
| Appleton, E. V       | FHM, I 4   | Benson, F W       | F, IV 4    |
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| Avery, O. T          | F, II. 4   | Buklé, H W        | F, III. 1  |
| Ayer, J B            | F, II 4    | Birkhoff, G D     | F, I 1     |
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| Bailey, I. W         | F, II. 2   | Blake, C H        | F, II 3    |
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| Bainbridge, K. T.    | F, I 2     | Blanchard, A A    | F, I. 3    |
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- Bolster, W F, III 1  
 Bonbright, J C F, III 3  
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 Warren, C H F, II 1  
 Warren, J F, III 1  
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 Webster, D L F, I 2  
 Webster, E S F, III 4  
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 Weyl, H FHM, I 1  
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 Wister, O F, IV 4  
 Wolbach, S B F, II 4  
 Wolff, J E F, II 1  
 Wolfsen, H A F, IV 3  
 Wolman, L F, III 3  
 Wood, R W F, I 2  
 Woods, F A F, II 3  
 Woods, F S F, I 1  
 Woodworth, R S F, IV 1  
 Worcester, J R F, I 4  
 Worrall, D E F, I 3  
 Wright, C H C F, IV 4  
 Wright, F E F, II 1  
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## STATUTES AND STANDING VOTES.

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### STATUTES.

*Adopted November 8, 1911 amended May 8, 1912, January 8, and May 14, 1913, April 14, 1915, April 12, 1916, April 10, 1918, May 14, 1919, February 8, April 12, and December 13, 1922, February 14, March 14, and October 10, 1923, March 10, 1926, May 9, 1928, April 8 and November 11, 1931, April 12, 1933, and February 14, 1934*

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### CHAPTER I THE CORPORATE SEAL

ARTICLE 1 The Corporate Seal of the Academy shall be as here depicted



ARTICLE 2 The Recording Secretary shall have the custody of the Corporate Seal

See Chap. v, art 3, chap vi, art. 2

## CHAPTER II.

### FELLOWS AND FOREIGN HONORARY MEMBERS AND DUES.

ARTICLE 1 The Academy consists of Fellows, who are either citizens or residents of the United States of America, and Foreign Honorary Members They are arranged in four Classes, according to the Arts and Sciences in which they are severally proficient, and each Class is divided into four Sections, namely:

#### CLASS I *The Mathematical and Physical Sciences*

- Section 1 Mathematics and Astronomy
- Section 2 Physics
- Section 3 Chemistry
- Section 4 Technology and Engineering

#### CLASS II *The Natural and Physiological Sciences*

- Section 1 Geology, Mineralogy, and Physics of the Globe
- Section 2 Botany
- Section 3 Zoölogy and Physiology
- Section 4 Medicine and Surgery

#### CLASS III *The Social Arts*

- Section 1 Jurisprudence
- Section 2 Government, International Law, and Diplomacy
- Section 3 Economics and Sociology
- Section 4 Administration and Affairs

#### CLASS IV *The Humanities*

- Section 1 Theology, Philosophy, and Psychology
- Section 2 History, Archaeology, and Anthropology
- Section 3 Philology
- Section 4 The Fine Arts and Belles Lettres

ARTICLE 2 The number of Fellows shall not exceed Eight hundred, of whom not more than Six hundred shall be residents of Massachusetts, nor shall there be more than Two hundred and twenty in any one Class.

ARTICLE 3 The number of Foreign Honorary Members shall not exceed One hundred and thirty They shall be chosen from among citizens of foreign countries most eminent for their discoveries and

attainments in any of the Classes above enumerated There shall not be more than Thirty-five in any one Class

ARTICLE 4. If any person, after being notified of his election as Fellow, shall neglect for six months to accept in writing, or, if a Fellow resident within fifty miles of Boston shall neglect to pay his Admission Fee, his election shall be void, and if any Fellow resident within fifty miles of Boston shall neglect to pay his Annual Dues for six months after they are due, provided his attention shall have been called to this Article of the Statutes in the meantime, he shall cease to be a Fellow, but the Council may suspend the provisions of this Article for a reasonable time

With the previous consent of the Council, the Treasurer may dispense (*sub silentio*) with the payment of the Admission Fee or of the Annual Dues or both whenever he shall deem it advisable In the case of officers of the Army or Navy who are out of the Commonwealth on duty, payment of the Annual Dues may be waived during such absence if continued during the whole financial year and if notification of such expected absence be sent to the Treasurer Upon similar notification to the Treasurer, similar exemption may be accorded to Fellows subject to Annual Dues, who may temporarily remove their residence for at least two years to a place more than fifty miles from Boston

If any person elected a Foreign Honorary Member shall neglect for six months after being notified of his election to accept in writing, his election shall be void

See Chap vii, art 2

ARTICLE 5 Every Fellow resident within fifty miles of Boston hereafter elected shall pay an Admission Fee of Ten dollars, unless previously as an Associate he has paid an Admission Fee of like amount

Every Fellow resident within fifty miles of Boston shall, and others may, pay such Annual Dues, not exceeding Fifteen dollars, as shall be voted by the Academy at each Annual Meeting, when they shall become due; but any Fellow shall be exempt from the annual payment if, at any time after his admission, he shall pay into the treasury Two hundred dollars in addition to his previous payments. Any Fellow shall also be exempt from Annual Dues who has paid such dues

for forty years, or, having attained the age of seventy-five has paid dues for twenty-five years

All Commutations of the Annual Dues shall be and remain permanently funded, the interest only to be used for current expenses

Any Fellow not previously subject to Annual Dues who takes up his residence within fifty miles of Boston, shall pay to the Treasurer within three months thereafter Annual Dues for the current year, failing which his Fellowship shall cease, but the Council may suspend the provisions of this Article for a reasonable time

Only Fellows who pay Annual Dues or have commuted them may hold office in the Academy or serve on the Standing Committees or vote at meetings

**ARTICLE 6** Fellows who pay or have commuted the Annual Dues and Foreign Honorary Members shall be entitled to receive gratis one copy of all Publications of the Academy issued after their election

*See Chap xi, art 2*

**ARTICLE 7** Diplomas signed by the President and the Vice-President of the Class to which the member belongs, and countersigned by the Secretaries, shall be given to Foreign Honorary Members and to Fellows on request

**ARTICLE 8** If, in the opinion of a majority of the entire Council, any Fellow or Foreign Honorary Member shall have rendered himself unworthy of a place in the Academy, the Council shall recommend to the Academy the termination of his membership, and if three-fourths of the Fellows present, out of a total attendance of not less than fifty at a Stated Meeting, or at a Special Meeting called for the purpose, shall adopt this recommendation, his name shall be stricken from the Roll

*See Chap iii, chap vi, art 1; chap x, art 1, 7, chap xi, art. 2*

### CHAPTER III

#### ELECTION OF FELLOWS AND FOREIGN HONORARY MEMBERS

The procedure in the election of Fellows and Foreign Honorary Members shall be as follows:

Nominations to Fellowship or Foreign Honorary Membership in any Section must be signed by Two Fellows of that Section, or by three Fellows of any Sections, and sent to the Corresponding Secretary ac-

accompanied by a statement of the qualifications of the nominee and brief biographical data

Notice shall be sent to every Fellow not later than the fifteenth of January in each year, reminding him that all nominations must be in the hands of the Corresponding Secretary before the fifteenth of February following

A list of the nominees, giving a brief account of each, with the names of the nominators, shall be sent to every Fellow with a request that he return the list with such confidential comments and indications of preference as he may choose to make

All the nominations, with any comments thereon and with expressions of preference on the part of the Fellows, shall be referred to the appropriate Class Committees, which shall canvass them, and report their recommendations in writing to the Council before the Stated Meeting of the Academy in April

Elections of Fellows and Foreign Honorary Members shall be made by the Council before the Annual Meeting in May, and announced at that meeting

Persons nominated in any year, but not elected, may be carried over to the list of nominees for the next year at the discretion of the Council, but shall not be further continued unless renominated

*See Chap ii, chap vi, art 1, chap x, art 1*

## CHAPTER IV

### OFFICERS

**ARTICLE 1** The Officers of the Academy shall be a President (who shall be Chairman of the Council), four Vice-Presidents (one from each Class), a Corresponding Secretary (who shall be Secretary of the Council), a Recording Secretary, a Treasurer, a Librarian, and an Editor, all of whom shall be elected by ballot at the Annual Meeting, and shall hold their respective offices for one year, and until others are duly chosen and installed

There shall be also sixteen Councillors, one from each Section of each Class. At each Annual Meeting four Councillors, one from each Class, shall be elected by ballot to serve for the full term of four years and until others are duly chosen and installed. The same Fellow shall not be eligible for two successive terms

The Councillors, with the other officers previously named, and the Chairman of the House Committee, *ex officio*, shall constitute the Council

See Chap xi, art 1

**ARTICLE 2** If any officer be unable, through death, absence, or disability, to fulfill the duties of his office, or if he shall resign, his place may be filled by the Council in its discretion for any part or the whole of the unexpired term

**ARTICLE 3** At the Stated Meeting in March, the President shall appoint a Nominating Committee of four Fellows having the right to vote, one from each Class. This Committee shall prepare a list of nominees for the several offices to be filled, and for the Standing Committees, and file it with the Recording Secretary not later than four weeks before the Annual Meeting

See Chap vi, art 2

**ARTICLE 4.** Independent nominations for any office, if signed by at least twenty Fellows having the right to vote, and received by the Recording Secretary not less than ten days before the Annual Meeting, shall be inserted in the call therefor, and shall be mailed to all the Fellows having the right to vote

See Chap vi, art 2

**ARTICLE 5** The Recording Secretary shall prepare for use in voting at the Annual Meeting a ballot containing the names of all persons duly nominated for office

## CHAPTER V

### THE PRESIDENT.

**ARTICLE 1** The President, or in his absence the senior Vice-President present (seniority to be determined by length of continuous Fellowship in the Academy), shall preside at all meetings of the Academy. In the absence of all these officers, a Chairman of the meeting shall be chosen by ballot.

**ARTICLE 2.** Unless otherwise ordered, all Committees which are not elected by ballot shall be appointed by the presiding officer.

**ARTICLE 3** Any deed or writing to which the Corporate Seal is to be affixed, except leases of real estate, shall be executed in the name of the Academy by the President or, in the event of his death, absence, or inability, by one of the Vice-Presidents, when thereto duly authorised

*See Chap ii, art 7; chap iv, art 1, 3, chap vi, art 2; chap vii, art. 1, chap x, art 6, chap xi, art 1, 2, chap xii, art 1*

## CHAPTER VI

### THE SECRETARIES.

**ARTICLE 1** The Corresponding Secretary shall conduct the correspondence of the Academy and of the Council, recording or making an entry of all letters written in its name, and preserving for the files all official papers which may be received At each meeting of the Council he shall present the communications addressed to the Academy which have been received since the previous meeting, and at the next meeting of the Academy he shall present such as the Council may determine

He shall notify all persons who may be elected Fellows or Foreign Honorary Members, send to each a copy of the Statutes, and on their acceptance issue the proper Diploma He shall also notify all meetings of the Council; and in case of the death, absence, or inability of the Recording Secretary he shall notify all meetings of the Academy

Under the direction of the Council, he shall keep a List of the Fellows and Foreign Honorary Members, arranged in their several Classes and Sections It shall be printed annually and issued as of the first day of July

*, See Chap ii, art 7, chap iii; chap iv, art 1, chap x, art 6; chap xi, art. 1, chap xii, art 1*

**ARTICLE 2** The Recording Secretary shall have the custody of the Charter, Corporate Seal, Archives, Statute-Book, Journals, and all literary papers belonging to the Academy

Fellows borrowing such papers or documents shall receipt for them to their custodian

The Recording Secretary shall attend the meetings of the Academy and keep a faithful record of the proceedings with the names of the Fellows present, and after each meeting is duly opened, he shall read the record of the preceding meeting

He shall notify the meetings of the Academy to each Fellow and by

mail at least seven days beforehand, and in his discretion may also cause the meetings to be advertised, he shall apprise Officers and Committees of their election or appointment, and inform the Treasurer of appropriations of money voted by the Academy

After all elections, he shall insert in the Records the names of the Fellows by whom the successful nominees were proposed

He shall send the Report of the Nominating Committee in print to every Fellow having the right to vote at least three weeks before the Annual Meeting

*See Chap iv, art 3*

In the absence of the President and of the Vice-Presidents he shall, if present, call the meeting to order, and preside until a Chairman is chosen

*See Chap i, chap ii, art 7, chap iv, art 3, 4, 5, chap x, art 6, chap xi, art 1, 2, chap xii, art 1, 3*

**ARTICLE 3** The Secretaries, with the Editor, shall have authority to publish such of the records of the meetings of the Academy as may seem to them likely to promote its interests

## CHAPTER VII

### THE TREASURER AND THE TREASURY

**ARTICLE 1** The Treasurer shall collect all money due or payable to the Academy, and all gifts and bequests made to it. He shall pay all bills due by the Academy, when approved by the proper officers, except those of the Treasurer's office, which may be paid without such approval, in the name of the Academy he shall sign all leases of real estate, and, with the written consent of a member of the Committee on Finance, he shall make all transfers of stocks, bonds, and other securities belonging to the Academy, all of which shall be in his official custody

He shall keep a faithful account of all receipts and expenditures, submit his accounts annually to the Auditing Committee, and render them at the expiration of his term of office, or whenever required to do so by the Academy or the Council

He shall keep separate accounts of the income of the Rumford Fund, and of all other special Funds, and of the Appropriation thereof, and render them annually

His accounts shall always be open to the inspection of the Council.

**ARTICLE 2** He shall report annually to the Council at its March meeting on the expected income of the various Funds and from all other sources during the ensuing financial year. He shall also report the names of all Fellows who may be then delinquent in the payment of their Annual Dues.

**ARTICLE 3** He shall give such security for the trust reposed in him as the Academy may require.

**ARTICLE 4** With the approval of a majority of the Committee on Finance, he may appoint an Assistant Treasurer to perform his duties, for whose acts, as such assistant, he shall be responsible, or, with like approval and responsibility, he may employ any Trust Company doing business in Boston as his agent for the same purpose, the compensation of such Assistant Treasurer or agent to be fixed by the Committee on Finance and paid from the Funds of the Academy.

**ARTICLE 5** At the Annual Meeting he shall report in print all his official doings for the preceding year, stating the amount and condition of all the property of the Academy entrusted to him, and the character of the investments.

**ARTICLE 6** The Financial Year of the Academy shall begin with the first day of April.

**ARTICLE 7** No person or committee shall incur any debt or liability in the name of the Academy, unless in accordance with a previous vote and appropriation therefor by the Academy or the Council, or sell or otherwise dispose of any property of the Academy, except cash or invested funds, without previous consent and approval of the Council.

See Chap ii, art 4, 5, chap vi, art 2, chap x, art 6, chap xi, art 1, 2, 3, chap xii, art 1

## CHAPTER VIII

### THE LIBRARIAN AND THE LIBRARY

**ARTICLE 1** The Librarian shall have charge of the printed books, keep a correct catalogue thereof, and provide for their delivery from the Library.

At the Annual Meeting, as Chairman of the Committee on the Library, he shall make a Report on its condition.

ARTICLE 2 In conjunction with the Committee on the Library he shall have authority to expend such sums as may be appropriated by the Academy for the purchase of books, periodicals, etc , and for defraying other necessary expenses connected with the Library

ARTICLE 3 All books procured from the income of the Rumford Fund or of other special Funds shall contain a book-plate expressing the fact

ARTICLE 4 Books taken from the Library shall be received for to the Librarian or his assistant

ARTICLE 5 Books shall be returned in good order, regard being had to necessary wear with good usage If any book shall be lost or injured, the Fellow to whom it stands charged shall replace it by a new volume or by a new set, if it belongs to a set, or pay the current price thereof to the Librarian, whereupon the remainder of the set, if any, shall be delivered to the Fellow so paying, unless such remainder be valuable by reason of association

ARTICLE 6 All books shall be returned to the Library for examination at least one week before the Annual Meeting

ARTICLE 7 The Librarian shall have the custody of the Publications of the Academy With the advice and consent of the President, he may effect exchanges with other associations

See Chap ii, art 6, chap xi, art 1, 2

## CHAPTER IX

### THE EDITOR AND THE PUBLICATIONS

ARTICLE 1 The Editor shall have charge of the conduct through the press of the Proceedings and the Memoirs, and all correspondence relative thereto, and shall have power to fix the price at which individual numbers of the Proceedings and Memoirs are sold

ARTICLE 2 In conjunction with the Committee of Publication, he shall have authority to expend such sums as may be appropriated by the Academy for printing the publications and for defraying other expenses therewith connected

ARTICLE 3 All publications which are financed in whole or in part from the income of the Rumford Fund or from the income of other

special funds, and all publications of work done with the aid of the Rumford Fund or other special funds, shall contain a conspicuous statement of this fact.

**ARTICLE 4.** Two hundred extra copies of each paper printed in the Proceedings or Memoirs shall be placed at the disposal of the author without charge

If, on account of the number of communications offered for publication, it shall be necessary to decline for publication communications otherwise acceptable, members of the Academy shall be given preference in each of the several Classes over non-members, but whenever it shall be necessary to exercise this preference, the Editor shall inform the Council of the fact

*See Chap iv, art 1; chap vi, art 3; chap x, art 6, chap xi, art 2, sect 4*

## CHAPTER X

### THE COUNCIL

**ARTICLE 1** The Council shall exercise a discreet supervision over all nominations and elections to membership, and in general supervise all the affairs of the Academy not explicitly reserved to the Academy as a whole or entrusted by it or by the Statutes to standing or special committees

It shall consider all nominations duly sent to it by any Class Committee, and act upon them in accordance with the provisions of Chapter III.

With the consent of the Fellow interested, it shall have power to make transfers between the several Sections, reporting its action to the Academy.

*See Chap iii, art 2, 3, chap xi, art 1*

**ARTICLE 2.** Nine members shall constitute a quorum

**ARTICLE 3** It shall establish rules and regulations for the transaction of its business, and provide all printed and engraved blanks and books of record.

**ARTICLE 4.** It shall act upon all resignations of officers, and all resignations and forfeitures of Fellowship, and cause the Statutes to be faithfully executed.

It shall appoint all agents and subordinates not otherwise provided for by the Statutes, prescribe their duties, and fix their compensation. They shall hold their respective positions during the pleasure of the Council.

ARTICLE 5. It may appoint, for terms not exceeding one year, and prescribe the functions of, such committees of its number, or of the Fellows of the Academy, as it may deem expedient, to facilitate the administration of the affairs of the Academy or to promote its interests.

ARTICLE 6 At its March meeting it shall receive reports from the President, the Secretaries, the Treasurer, and the Standing Committees, on the appropriations severally needed for the ensuing financial year. At the same meeting the Treasurer shall report on the expected income of the various Funds and from all other sources during the same year.

A report from the Council shall be submitted to the Academy, for action, at the March meeting, recommending the appropriation which in the opinion of the Council should be made.

On the recommendation of the Council, special appropriations may be made at any Stated Meeting of the Academy, or at a Special Meeting called for the purpose.

*See Chap xi, art 3*

ARTICLE 7 After the death of a Fellow or Foreign Honorary Member, it shall appoint a member of the Academy to provide a biographical notice for publication in the Proceedings.

ARTICLE 8 It shall report at every meeting of the Academy such business as it may deem advisable to present.

*See Chap ii, art 4, 5, 8, chap iv, art 1, 2, chap vi, art 1, chap vii, art 1, chap xii, art 1, 4.*

## CHAPTER XI

### STANDING COMMITTEES.

ARTICLE 1 The Class Committee of each Class shall consist of the Vice-President, who shall be chairman, and the four Councillors of the Class, together with such other officer or officers annually elected as may belong to the Class. It shall consider nominations to Fellowship.

in its own Class, and report in writing to the Council such as may receive at a Class Committee Meeting a majority of the votes cast, provided at least three shall have been in the affirmative

See Chap iii, art 2

ARTICLE 2 At the Annual Meeting the following Standing Committees shall be elected by ballot to serve for the ensuing year

(i) *The Committee on Finance*, to consist of four Fellows, who, through the Treasurer, shall have full control and management of the funds and trusts of the Academy, with the power of investing the funds and changing the investments thereof in their discretion.

See Chap iv, art 3, chap vii, art 1, 4, chap x, art 6

(ii) *The Rumford Committee*, to consist of seven Fellows, who shall report to the Academy on all applications and claims for the Rumford Premium It alone shall authorize the purchase of books, publications and apparatus at the charge of the income from the Rumford Fund, and generally shall see to the proper execution of the trust

See Chap iv, art 3; chap x, art 6

(iii) *The Cyrus Moors Warren Committee*, to consist of seven Fellows, who shall consider all applications for appropriations from the income of the Cyrus Moors Warren Fund, and generally shall see to the proper execution of the trust

See Chap iv, art 3; chap x, art 6

(iv) *The Committee of Publication*, to consist of the Editor, *ex officio*, as Chairman, and four other Fellows, one from each Class, to whom all communications submitted to the Academy for publication shall be referred, and to whom the printing of the Proceedings and the Memoirs shall be entrusted

It shall fix the price at which volumes of the publications shall be sold, but Fellows may be supplied at half price with volumes which they are not entitled to receive gratis.

It shall determine when the pressure of material offered for publication makes it necessary to give preference to members of the Academy as compared with non-members, or to give priority to certain members as compared with others, and to what extent this preference or priority shall be applied in each of the four Classes, to the

end that a proper balance of the facilities of publication with respect to subject matter and authors may be maintained

*See Chap iv, art 3; chap vi, art 1, 3, chap ix; chap x, art. 6.*

(v) *The Committee on the Library*, to consist of the Librarian, *ex officio*, as Chairman, and four other Fellows, one from each Class, who shall examine the Library and make an annual report on its condition and management

*See Chap iv, art 3, chap viii, art 1, 2, chap x, art 6*

(vi) *The House Committee*, to consist of four Fellows, who shall have charge of all expenses connected with the House, including the general expenses of the Academy not specifically assigned to the care of other Committees or Officers

*See Chap iv, art 1, 3, chap x, art 6*

(vii) *The Committee on Meetings*, to consist of the President, the Recording Secretary, and four other Fellows, who shall have charge of plans for meetings of the Academy

*See Chap iv, art 3, chap x, art 6*

(viii) *The Auditing Committee*, to consist of two Fellows, who shall audit the accounts of the Treasurer, with power to employ an expert and to approve his bill

*See Chap iv, art 3, chap vii, art 1, chap x, art 6*

(ix) *The Committee on Biographical Notices*, to consist of six Fellows, two to be elected each year, six in 1933, one of them to be a Secretary of the Academy, to see that biographical notices of the Fellows are provided

*See Chap x, art 7*

**ARTICLE 3** The Standing Committees shall report annually to the Council in March on the appropriations severally needed for the ensuing financial year; and all bills incurred on account of these Committees, within the limits of the several appropriations made by the Academy, shall be approved by their respective Chairmen.

In the absence of the Chairman of any Committee, bills may be approved by any member of the Committee whom he shall designate for the purpose.

*See Chap vii, art 1, 7; chap. x, art 6.*

## CHAPTER XII

### MEETINGS, COMMUNICATIONS, AND AMENDMENTS

**ARTICLE 1** There shall be annually eight Stated Meetings of the Academy, namely, on the second Wednesday of October, November, December, January, February, March, April, and May Only at these meetings, or at adjournments thereof regularly notified, or at Special Meetings called for the purpose, shall appropriations of money be made or amendments of the Statutes or Standing Votes be effected

The Stated Meeting in May shall be the Annual Meeting of the Corporation.

Special Meetings shall be called by either of the Secretaries at the request of the President, of a Vice-President, of the Council, or of ten Fellows having the right to vote, and notifications thereof shall state the purpose for which the meeting is called

A meeting for receiving and discussing literary or scientific communications may be held on the fourth Wednesday of each month, excepting July, August, and September, but no business shall be transacted at said meetings

**ARTICLE 2** Twenty-five Fellows having the right to vote shall constitute a quorum for the transaction of business at Stated or Special Meetings Eighteen Fellows shall be sufficient to constitute a meeting for literary or scientific communications and discussions

**ARTICLE 3** Upon the request of the presiding officer or the Recording Secretary, any motion or resolution offered at any meeting shall be submitted in writing

**ARTICLE 4** No report of any paper presented at a meeting of the Academy shall be published by any Fellow without the consent of the author; and no report shall in any case be published by any Fellow in a newspaper as an account of the proceedings of the Academy without the previous consent and approval of the Council The Council, in its discretion, by a duly recorded vote, may delegate its authority in this regard to one or more of its members.

**ARTICLE 5.** No Fellow shall introduce a guest at any meeting of the Academy until after the business has been transacted, and especially until after the result of the balloting upon nominations has been declared.

**ARTICLE 6** The Academy shall not express its judgment on literary or scientific memoirs or performances submitted to it, or included in its Publications

**ARTICLE 7** All proposed Amendments of the Statutes shall be referred to a committee, and on its report, at a subsequent Stated Meeting or at a Special Meeting called for the purpose, two-thirds of the ballot cast, and not less than twenty-five, must be affirmative to effect enactment

**ARTICLE 8** Standing Votes may be passed, amended, or rescinded at a Stated Meeting, or at a Special Meeting called for the purpose, by a vote of two-thirds of the members present They may be suspended by a unanimous vote

*See Chap ii, art 5, 8, chap iii, chap iv, art 3, 4, 5, chap v, art 1, chap vi, art 1, 2; chap x, art 8*

## STANDING VOTES.

1. Communications of which notice has been given to either of the Secretaries shall take precedence of those not so notified

2. Fellows may take from the Library six volumes at any one time, and may retain them for three months, and no longer. Upon special application, and for adequate reasons assigned, the Librarian may permit a larger number of volumes, not exceeding twelve, to be drawn from the Library for a limited period

3. Works published in numbers, when unbound, shall not be taken from the Hall of the Academy without the leave of the Librarian

4. The Council, under such rules respecting nominations as it may prescribe, may elect as Associates of the Academy a limited number of men of mark in affairs or of distinguished service in the community

Associates shall be entitled to the same privileges as Fellows, but shall not have the right to vote

The admission fee and annual dues of Associates shall be the same as those of Fellows residing within fifty miles of Boston

5. Communications offered for publication in the Proceedings or Memoirs of the Academy shall not be accepted for publication before the author shall have informed the Committee on Meetings of his readiness, either himself or through some agent, to use such time as the Committee may assign him at such meeting as may be convenient both to him and to the Committee, for the purpose of presenting to the Academy a general statement of the nature and significance of the results contained in his communication

## RUMFORD PREMIUM.

In conformity with the terms of the gift of Sir Benjamin Thompson, Count Rumford, of a certain Fund to the American Academy of Arts and Sciences, and with a decree of the Supreme Judicial Court of Massachusetts for carrying into effect the general charitable intent and purpose of Count Rumford, as expressed in his letter of gift, the Academy is empowered to make from the income of the Rumford Fund, as it now exists, at any Annual Meeting, an award of a gold and a silver medal, being together of the intrinsic value of three hundred dollars, as a Premium to the author of any important discovery or useful improvement in light or heat, which shall have been made and published by printing, or in any way made known to the public, in any part of the continent of America, or any of the American islands, preference always being given to such discoveries as, in the opinion of the Academy, shall tend most to promote the good of mankind, and, if the Academy sees fit, to add to such medals, as a further Premium for such discovery and improvement, a sum of money not exceeding three hundred dollars.

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